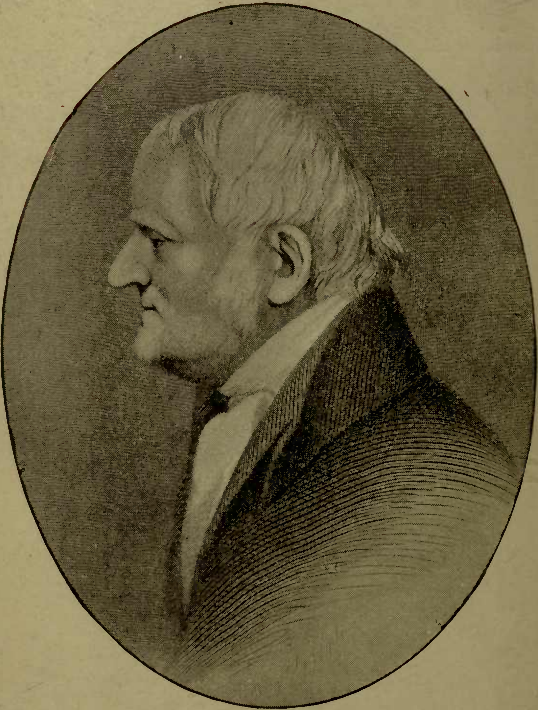
THE TEMPLE PRIMERS

MODERN CHEMISTRY

Systematic

By

WILLIAM RAMSAY, D.Sc.



JOHN DALTON

MODERN CHEMISTRY

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MODERN CHEMISTRY

SECOND PART

SYSTEMATIC CHEMISTRY

CHAPTER I

Methods of Preparing Elements—Their Physical Properties.

Mixtures and Compounds.—In the olden days, no distinction was drawn between a compound and a mixture. Indeed, all "impure" substances artificially prepared were termed "mixts." It was only after the true idea of elements had been arrived at, and indeed not until Dalton had formulated the laws which go by his name, that the distinction was drawn. The ultimate criterion for combination is definiteness of proportion, and this is generally connected with uniformity in properties, or homogeneity. A substance is said to be homogeneous when no one part of it differs from any other part in composition. But this may be predicated of glass, or of air, which are mixtures, and not compounds. A mixture *may* be homogeneous; a compound *must*.

Again, it is usually accepted that the separation of the constituents of a mixture may be effected by mechanical, or at least by physical means; whereas the separation of the elements from a compound require chemical treatment. Here it is difficult to draw a sharp distinction. The separation of carbon dioxide from soda-water by the application of heat is similar in character to the separation of sugar from water by evaporation of the water; yet we believe that a solution of carbon dioxide in water constitutes a compound, while that of sugar in water is a mere mixture of the two. It is necessary to be guided by analogy in the former case; and it is probable that the compound named carbonic acid is really contained in a solution of carbon dioxide in water, on account of the formulæ and behaviour of the carbonates.

The Atmosphere.—In the case of mixtures of gases, the problem becomes an easier one. For in this case, each gas retains its individual properties. The atmosphere, for example, is believed to be a mixture of the gases

Nitrogen, . .	78.16	per cent.
Oxygen, . .	20.90	,,
Argon, &c., . .	0.94	,,
	100.00	

if small amounts of water-vapour, of carbon dioxide, and of ammonia, all of which vary considerably in amount, be subtracted.

This can be shown by several lines of argument.

First, The density of air agrees with the mean of the densities of its constituents, taken in the proportion in which they occur. Thus, the density of the mixture of atmospheric nitrogen and argon differs by only 1 part in 40,000 from that calculated from their relative weights, and the proportion in which they occur. This is the case with compound gases only when the constituents are present in equal proportions by volume, as in hydrogen chloride, HCl. The above mixture is far from fulfilling that requirement.

Second, The constituents of air can be separated by diffusion. **Thomas Graham** discovered that the rate of escape of gases through an opening, or of passage through a porous partition is inversely in the order of the square roots of their relative densities. Now, air has been enriched in oxygen and in argon by diffusion; the lighter nitrogen passes more rapidly in the proportion of $\frac{1}{\sqrt{14}} : \frac{1}{\sqrt{16}} : \frac{1}{\sqrt{20}}$, the last two fractions referring to the rates of oxygen and argon respectively; the oxygen and argon, being more slowly diffusible, are left to the last.

Third, The constituents of air may be separated by solution in water. While oxygen is soluble at atmospheric temperature in the proportion of about 3 volumes in 100 of water, nitrogen is much less soluble—about 1.5 volumes; and argon about 4.1 volumes. Hence, on shaking air with water, the relative volumes dissolved are:

$$\text{Oxygen, } 3 \times 20.90\text{; Nitrogen, } 1.5 \times 78.16\text{; and Argon, } 4.1 \times 0.94,$$

or in the proportion of 63 : 117 : 3.8. It is evident that the relative proportion of nitrogen has considerably decreased.

Fourth, The elements contained in air are not present in any atomic ratio. To ascertain the relative number of atoms of these elements it is necessary to divide the percentage amount of each by its atomic weight; thus we have

$$\text{Nitrogen, } \frac{78.16}{14} = 5.58\text{; Oxygen, } \frac{20.9}{16} = 1.31\text{;}$$
$$\text{Argon, } \frac{0.94}{40} = 0.024\text{;}$$

and these numbers bear to each other no simple ratio.

Lastly, it is possible by distilling liquid air to separate the more volatile nitrogen from the less volatile oxygen and argon.

For these reasons, and other similar ones, it is concluded that air is a mixture.

The Analysis of the Atmosphere is, however, always performed by chemical means, for the difference in physical properties of its constituents is not sufficiently marked to allow of their being utilised for purposes of separation. Many common elements unite easily with oxygen to form non-volatile compounds, when they are heated in air. One of the most convenient for this purpose is metallic copper. By passing a known volume of air over copper turnings, contained in a counterpoised tube of hard glass, and heated to redness, the oxygen of the air is removed, for it combines with the copper to form non-volatile black oxide of copper. The increase in weight of this tube gives the weight of the oxygen in the measured volume of air. But it is customary to analyse air volumetrically by absorbing the oxygen from a known volume by means of burning phosphorus, or of a solution of potassium pyrogallate : the remainder consists of a mixture of nitrogen, argon and its congeners. The separation of these gases from each other is described in the next paragraph.

Reference has already been made in Part I. to the different processes which may be used for the isolation of elements from their compounds. But there exists a group of elements, that of which the first member is helium, which form no compounds, and which therefore are found only in a free state. It is, therefore, convenient to begin with these.

The HELIUM Group.—These elements are all gases at the ordinary temperature of the atmosphere, and they are consequently all to be found in atmospheric air. They are colourless, even in the liquid condition, and are devoid of smell and taste. They are very sparingly soluble in water ; for example, 100 volumes of water dissolve only 4.1 volumes of argon at 15°. Their preparation consists, first, in the separation of the other constituents of air from them, and, second, in their separation from each other.

Air, which is a mixture, and not a compound, of nitrogen, oxygen, carbon dioxide, ammonia, water-vapour, and the gases of the helium group, is a supporter of combustion, owing to the combination of the oxygen which it contains with most other elements. Now, when air passed through a tube full of a mixture of caustic soda and lime, to remove carbon dioxide, and then through a U-tube containing sulphuric acid, to deprive it of water-vapour and ammonia, is led over red-hot copper, or over some other red-hot metal which unites with oxygen, the oxygen is retained, and nitrogen with members of the helium group alone passes on. The nitrogen can be removed in one of two ways. The first plan is due to **Cavendish**, who attempted to prove that atmospheric nitrogen was a homogeneous substance. He mixed atmospheric nitrogen with oxygen, and passed electric sparks through the mixture, having a little caustic soda present in the tube. Under the influence of the sparks, the nitrogen and oxygen combine, giving nitride peroxide, NO_2; this compound is absorbed by the soda, with formation of sodium nitrate and nitrite, $NaNO_3$ and $NaNO_2$. Cavendish obtained a residue of not more than one-hundred-and-twentieth of the nitrogen; and he concluded that if atmospheric nitrogen was not homogeneous, it contained only a trace of another gas. The second plan is to pass the atmospheric nitrogen over red-hot magnesium, or, better, over a mixture of magnesium powder and lime, which gives calcium; the magnesium or the calcium unites with the nitrogen, and the inert gases pass on.

To separate these gases from each other, they are compressed into a bulb, cooled to -185° by being immersed in liquid air. The **argon, krypton**, and **xenon** condense to a liquid, in which the **neon** and **helium** are dissolved. On removing the bulb from the liquid air, its temperature rises, and the helium and neon escape first, mixed with a large amount of argon. Argon distils next, and krypton and xenon remain till the last. By frequently repeating this process of "fractional distillation," the argon, krypton, and xenon can be separated from each other, and from the helium and neon which still remain mixed with each other, for both are gases at the temperature of boiling air.

To separate helium from neon, recourse must be had to liquid hydrogen. To liquefy hydrogen, the process is in principle the same as that for liquefying air, described on p. 26. The hydrogen, compressed by a pressure of 200 atmospheres, is cooled to −205° by passing through a coil of copper pipe, immersed in liquid air boiling under low pressure. On expanding, its temperature is still further lowered, and the still colder gas, in passing upwards, cools the tubes through which the compressed gas is passing. The hydrogen finally issues in the liquid state, as a colourless, mobile liquid, of the approximate temperature −240°. By its aid, if a mixture of neon and helium is cooled to −240°, the former freezes, while the latter remains gaseous. The gaseous helium can be removed with the pump; and the neon, after it has been warmed, may also be pumped off in a pure state.

Helium can also be prepared by heating certain specimens of pitchblende or uraninite, a mineral consisting chiefly of oxide of uranium. The gas, which appears to exist in some sort of combination with the uranium oxide, escapes; it contains a trace of argon. All these gases give very striking spectra, and that of helium was observed during the solar eclipse of 1868 in the chromosphere, or coloured atmosphere, of the sun. Although at that time it had not been discovered on the earth, the name "helium" was given to the bright yellow line, which is the most characteristic of its spectrum.

As regards the relative amount of these gases contained in air, 100 volumes of air contain 0.937 volume of the mixture. By far the largest portion of this mixture is argon; probably the volume of all the others taken together does not exceed one-four-hundredth part of that of the argon. Indeed, it may be said with truth that there is less xenon in air than there is gold in sea-water.

Methods of Separating Elements from their Compounds.—The methods of preparation of the remaining elements depend on considerations of the cost of the compound from which the element is to be prepared, and on the ease of preparation. In the case of those elements which are required on a commercial scale, like iron, for example, the process of manufacture is regulated chiefly by the cost of the ore, and of the operations necessary to produce the metal in a state of purity sufficient for commercial purposes. But if perfectly pure iron is required for scientific purposes—for example, in order to determine its electrical properties—then the question of cost does not come into consideration, and processes are adopted which are necessarily very costly. In the description which follows, however, we shall give only the ordinary methods of preparation.

Again, the process chosen depends greatly on the physical and chemical properties of the element which it is desired to isolate. Some elements are volatile, and are more or less easily separated by distillation from the material from which they are produced ; some elements are attacked by water, while others resist attack ; some fuse at comparatively low temperatures, and can thus be separated, while others are producible in a compact state only at the enormously high temperature of the electric arc. It is necessary, therefore, to know the properties of the element required before deciding on a process for its isolation. The preparation of the remaining elements will therefore be considered from this point of view.

(1) Separation of the element by means of an electric current.

(*a*) **From a fused salt.**—One condition is that the salt shall fuse at a convenient temperature—that is, at or below a red heat. Another is that, in the case of metals which are commercially used, the salts must be cheaply obtainable, and the metals easily separated from the salts.

It is interesting to note that this process led, in the hands of **Sir Humphry Davy**, to the discovery of the metals of the alkalies, potassium and sodium; he first prepared them by passing a current from a battery of high voltage through the hydroxide, melted on a piece of platinum foil. The metal was visible only for an instant; for it floated up from the electrode of platinum wire, and burst into flame as soon as it came into the air.

As a rule, however, the chlorides are the most convenient salts for electrolysis. From the known fact that the melting-point of a compound is lowered by the presence of an "impurity," it is often found advantageous to electrolyse a mixture of chlorides rather than a pure chloride; in this case one of the elements is liberated in preference to the other. As the anode has to withstand the action of chlorine, it is always made of carbon, which does not unite with chlorine directly; the kathode may be of iron, a metal which has no tendency to form alloys with those which are prepared in this way, at least at the temperatures required. The kathode may be the iron pot in which the chloride is kept fused.

The elements which are prepared in this way are: lithium, sodium, potassium, rubidium, cæsium, beryllium, magnesium, calcium, strontium, and barium. The first five are easily fusible white soft metals, which take fire when heated in air, and must therefore be kept in an atmosphere free from oxygen; they also attack water, liberating hydrogen, with formation of the hydroxide MOH. Their density is so low that they float on their fused chlorides; they must, therefore, be liberated in the interior of a bell-shaped iron electrode or of a fireclay receptacle, down which an iron kathode passes. Beryllium and magnesium are better prepared from a mixture of their chlorides with potassium chloride; the latter melts and collects at the bottom of the pot, which, in this case, may be the kathode. They are hard white metals, magnesium melting at about 750°, and beryllium about 1200°. They, too, take fire when heated in air, and burn with a brilliant flame; indeed, the chief use of magnesium is for signalling purposes. The metal is drawn, while hot, into wire, which is then rolled into ribbon; this ribbon burns with an exceedingly bright flame, producing the oxide MgO. Calcium, strontium, and barium are also white metals; they have been produced by electrolysis of their cyanides, $M(CN)_2$, compounds which fuse at a lower temperature than the chlorides. They are very readily attacked by water, yielding the hydroxides $M(OH)_2$. The only two of these metals which find commercial use are sodium and magnesium.

Aluminium, which is also manufactured on a large scale, is produced from its ore, bauxite, from which pure alumina, the oxide, is first prepared. The alumina is dissolved in fused cryolite, a fluoride of aluminium and sodium of the formula Na_3AlF_6, deposits of which occur in Greenland. The aluminium sinks to the bottom of the crucible, and when a sufficient quantity accumulates it is tapped out. The "flux," as the cryolite is termed, is again melted, and a further quantity of alumina is dissolved in it. The metal is fairly hard, white, susceptible of a high polish, ductile and malleable. It is also very light (about two and a half times as heavy as water), and not easily oxidised in air at the ordinary temperature, nor is it attacked by water.

(*b*) **From a dissolved salt.**—Gallium, a tin-white, hard metal, very rare, contained in some zinc ores, is deposited from a solution of its hydroxide in caustic potash. Copper prepared, as will be seen below, in a crude state by displacement, is purified by electrolysis. It is of the utmost importance to employ pure copper for the conduction of electric currents; for although copper is one of the best conductors, its resistance is enormously increased by the presence of a very small trace of impurity. To purify it, large rectangular blocks of crude copper are suspended close to thin sheets of pure copper in an acid bath of copper sulphate, $CuSO_4.Aq$. The heavy block is made the anode and the thin sheet the cathode; the *sulphation*, $\overset{--}{SO_4}$, in discharging at the anode, dissolves copper from the thick block as sulphate; while the *cuprion*, $\overset{++}{Cu}$, in yielding up its charge at the kathode, deposits on the latter and increases its thickness. The impurities, arsenic, antimony, and iron, remain in solution, and a sludge is deposited containing silver and gold, besides traces of many other elements. Copper is a very malleable, ductile red metal, melting at 1330°.

Objects of iron are often "nickel-plated," or covered with a thin film of nickel, a white, hard metal which preserves its lustre in air, for it is not easily oxidisable. This is done by making the object to be coated with nickel the kathode and a bar of nickel the anode; the liquid is a solution of oxalate of nickel and potassium. Iron objects are first coated with copper before nickelling. Silver and gold are best deposited from their double cyanides with potassium; these salts are used because the deposit is harder and more uniform than if a halide be used. In thus coating objects, it is of importance that the current density, *i.e.* the ratio of the current to the area of the surface of the object to be coated, should be considered; if this be too high, the metal will be deposited in a loose, flocculent condition.

As an illustration of the changes which take place during such electrolysis, the deposition of silver may be chosen. The compound employed is, as stated, the double cyanide (see p. 187); its formula is $KAg(CN)_2$, and the ions are $\overset{+}{K}$ and $Ag(\overset{-}{C}N)_2$. There are, however, at the same time a few ions of $\overset{+}{Ag}$ and $\overset{-}{CN}$. From the last, metallic silver is deposited on the kathode; and as soon as its amount is reduced, a fresh quantity is formed by the decomposition of the complex ion, $Ag(\overset{-}{C}N)_2$. The formation and deposition of the silver ion goes on continuously until all the silver required has been deposited. Similar changes take place during the electro-deposition of nickel and of gold.

Modern electrolytic processes for obtaining chlorine and caustic soda ($NaOH$) from salt result in the liberation of enormous quantities of hydrogen. The salt, dissolved in water, is placed in a tank divided into two compartments by a porous diaphragm; the anode, which consists of carbon rods, dips into one, and the kathode, which may be formed of copper plates, in the other. The ions, of course, are $\overset{+}{\mathrm{Na}}.\mathrm{Aq}$, and $\overset{-}{\mathrm{Cl}}.\mathrm{Aq}$. The chlorine is liberated at the anode, and the sodium at the kathode. But as soon as the sodion is discharged, it reacts with the water, forming caustic soda, thus: $2Na + 2HOH = 2NaOH + H_2$. Hence the production of hydrogen. Bromine and iodine may be liberated in the same way as chlorine, the bromide or iodide of sodium or potassium being substituted for the chloride. As fluorine at once acts on water, liberating oxygen in the form of ozone, O_3, it cannot be produced from an aqueous solution of a fluoride; but it has been found that liquid hydrogen fluoride has ionising power, so that on passing a current between poles of platinum-iridium (an alloy of metals which is less attacked by fluorine than any other conductor) through a solution of hydrogen-potassium fluoride, HKF, in pure liquid hydrogen fluoride, H_2F_2, at $-30°$, fluorine is evolved from the anode as a pale yellow gas with a strong characteristic smell, somewhat resembling that of the other halogens, chlorine, bromine, and iodine; while hydrogen is evolved at the kathode, having been produced by the action of the potassium on the hydrogen fluoride. Fluorine boils at $-195°$, chlorine at $-35°$, bromine at 59°, and iodine, which is a solid at atmospheric temperature, melts at 114° and boils at 184°. The colours of these elements also show a gradation. Chlorine is greenish-yellow; bromine, red both as gas and liquid; iodine is a blue-black solid and a violet gas. These three elements are somewhat soluble in water, and more so in a solution of their soluble salts. It has recently been found that another ionising agent than water may be used. Lithium chloride is soluble in pyridine, a compound of the formula C_5H_5N, and may be electro-deposited on a platinum kathode from such a solution.

The metal is not attacked by pyridine; the chlorine, however, is rapidly absorbed.

(2) Separation of an element from a compound by rise of temperature.

This method is applied in practice only to the preparation of oxygen, and of chlorine, bromine, and iodine; but many other elements may be thus made, where the compound heated does not tend to re-form on cooling. These cases will be considered first.

Ordinary coal-gas consists chiefly of methane, CH_4, ethylene, C_2H_4, carbon monoxide, CO, and hydrogen, the last amounting to nearly 50 per cent. of the volume of the gas. This hydrogen owes its origin, at least in part, to the decomposition of its compounds with carbon, by their coming into contact with the red-hot walls of the retort in which the coal is distilled. Carbon deposits in a dense black mass on the iron, and is removed from time to time with a chisel. Hydrogen escapes and mixes with the coal-gas. This form of carbon is used for the pencils for arc-lights, and for the anodes of Bunsen's and other forms of cells, and also for anodes in electro-chemical processes.

The compounds of hydrogen with nitrogen (ammonia, NH_3), sulphur, selenium, and tellurium (sulphuretted, seleniuretted, or telluretted hydrogen, H_2S, H_2Se, H_2Te), all of which are gases at the ordinary temperature, are decomposed if passed through a red-hot tube, giving hydrogen, which escapes along with nitrogen if ammonia be heated; or a deposit of the sulphur, &c., in the cold part of the tube if one of the other gases mentioned be employed.

The oxides of the metals ruthenium, rhodium, palladium, silver, osmium, iridium, platinum, gold, and mercury are decomposed at a red heat; and the chlorides, bromides, iodides, and sulphides are also decomposed, except those of silver and mercury.

But none of these methods are practical plans of preparing the elements. On the other hand, as already stated, this method is generally used for the production of oxygen. This gas, although it had probably been obtained in an impure state by the older experimenters, was first produced in approximate purity by **Priestley** and simultaneously by **Scheele** in 1774. Priestley produced it by heating mercuric oxide, HgO, which decomposes thus: $2HgO = 2Hg + O_2$. And **Lavoisier** showed that it was possible to produce mercuric oxide by heating mercury to its boiling-point in a confined portion of air, and by separating and weighing the oxide, and subsequently heating it till it decomposed again, he proved that the oxygen had really been extracted from the air.

Certain oxides are not wholly decomposed into oxygen and element when heated, but leave an oxide containing less oxygen than that originally heated. Among these is black manganese dioxide, a mineral named pyrolusite; $3MnO_2 = Mn_3O_4 + O_2$. Lead dioxide undergoes a similar change: $2PbO_2 = 2PbO + O_2$. The most important application of this method, however, is the commercial plan of producing oxygen carried out in the "Brin Company's" works. In their process, barium oxide, BaO, is heated in iron tubes under pressure, air being pumped in. The barium oxide absorbs the oxygen of the air, the nitrogen being allowed to escape. After the operation has gone on for about five minutes, a considerable amount of oxygen is absorbed, barium dioxide, BaO_2, being formed. The stopcocks of the pipes leading to the pump are then reversed, so that gas is exhausted from the hot iron tubes. When the pressure is reduced, the barium dioxide loses oxygen, and again returns to the state of monoxide: $2BaO_2 = 2BaO + O_2$. The pumping is continued for about five minutes, and the valves are again reversed. The process is thus a continuous one; the oxygen is not pure, for it contains about 7 per cent. of nitrogen; but for medical use in cases of pneumonia, and for the oxy-hydrogen blowpipe, its purity is sufficient.

This method of preparing oxygen is an instance of what is termed "mass-action." The temperature is kept constant, but the pressure is raised when it is desired to cause the oxide to absorb oxygen, and lowered when it is necessary to remove the oxygen. When pressure is raised, the number of molecules of oxygen in unit volume of the space (or the mass) is increased, and hence the number in contact with the absorbing medium, the barium oxide. Combination, therefore, takes place between the two. On reducing pressure, the number per unit volume is reduced, and the compound decomposes. The phenomenon is analogous with the behaviour of a vapour when it is compressed; after a certain pressure has been reached—the vapour pressure—the vapour condenses to a liquid, and if more vapour be compressed into the same space, the pressure does not rise further, but more vapour is condensed: this is analogous to the formation of more BaO_2. On pumping out vapour, the pressure does not fall, but the liquid evaporates: this is the analogue of the decomposition of the BaO_2 into BaO. The law of mass-action is very generally applicable.

Certain oxides, for instance, pentoxide of iodine, I_2O_5, and of nitrogen, N_2O_5, decompose when heated. These oxides form combinations with the oxides of many other elements, such as sodium or potassium oxide, *e.g.* $Na_2O.I_2O_5$ or $NaIO_3$, $K_2O.N_2O_5$ or KNO_3; a similar compound is potassium chlorate, $KClO_3$ or $K_2O.Cl_2O_5$, although the simple oxide of chlorine is unknown. Now, potassium and sodium oxides are not decomposed by heat, and when these salts are heated oxygen is evolved from the pentoxide of chlorine or iodine. These elements, however, do not escape, but replace the oxygen combined with the sodium or potassium, forming chloride of the metal, thus: $K_2O.Cl_2O_5 = K_2O + Cl_2 + 5O$, and $K_2O + Cl_2 = 2KCl + O$, or, summing up both changes in one equation, $2KClO_3 = 2KCl + 3O_2$. Nitrate of potassium, on the other hand, loses only one atom of oxygen, leaving nitrite: $2KNO_3 = 2KNO_2 + O_2$.

Oxygen is a colourless gas, without smell or taste; it can be liquefied, at a high pressure and a low temperature, to a pale blue liquid boiling at −182°. Most elements unite directly with it, often with such a rise of temperature that incandescence is produced; in such a case the phenomenon is termed "combustion." In many instances, for example when iron rusts, the oxidation is not attended by any measurable rise of temperature, although in all cases heat is evolved, but in some cases extremely slowly.

Chlorine, bromine, and iodine are generally prepared by heating together a chloride, bromide, or iodide with manganese dioxide and sulphuric acid diluted with water. Here the first change is the formation of the halogen hydride, HCl, HBr, or HI. The hydride, however, is ionised in water, and the $\overset{+}{H}\overset{-}{Cl}.Aq.$, for example, at once reacts with the MnO_2, forming non-ionised water and $MnCl_4.Aq$, thus: $MnO_2 + 4\overset{+}{H}\overset{-}{Cl}.Aq. = \overset{++++}{Mn}\overset{-}{Cl_4}.Aq. + 2H_2O$. Tetrad manganese, however, appears not to be able to co-exist with chlorine in solution; hence the manganese loses an electron and becomes $\overset{+++}{Mn}$, the lost charge neutralising one of the charged chlorine ions, which escapes in an electrically neutral state. Even then, however, the $\overset{+++}{Mn}$, though capable of existence at low temperature, still loses a charge, and a second chlorine atom is liberated in a non-ionised state. Hence the whole change is: $\overset{++++}{Mn}\overset{-}{Cl_4}.Aq. = \overset{++}{Mn}\overset{-}{Cl_2}.Aq. + Cl_2$. Summing all these changes in one equation, we have: $MnO_2 + 2NaCl.Aq. + 2H_2SO_4.Aq. = MnSO_4.Aq. + Na_2SO_4.Aq. + 2H_2O + Cl_2$; or, if hydrochloric acid alone be warmed with manganese dioxide, $MnO_2 + 4HCl.Aq. = MnCl_2.Aq. + 2H_2O + Cl_2$.

(3) **Separation of an element from a compound by displacement.**—This is by far the most general method

of preparing elements. The elements commonly used as displacing agents are:—

(*a*) **Hydrogen at a red heat.**—The oxide or chloride is placed in a tube of hard glass, heated to 600° or 700° in a tube-furnace, and a stream of dry hydrogen is passed through the tube. Water or hydrogen chloride is formed, and is carried on by the current of hydrogen, and the element is left. Indium, thallium, germanium, tin, lead, antimony, and bismuth are left in fused globules, solidifying to white lustrous metallic beads; arsenic gasifies and condenses in the unheated part of the tube as a grey deposit; tellurium, which is also volatile, condenses as a lustrous metallic solid; while iron, cobalt, nickel, copper, and silver do not fuse at that temperature. The first three remain as grey powders, the copper as a red powder, and the silver in a white spongy condition. These metals can be fused by heating them in a crucible to a sufficiently high temperature; it is well to use a "flux," or substance to make them flow, such as sodium carbonate or borax; the flux fuses, and dissolves any film of oxide off the surface of the metallic beads, and they then join up to form a single mass of molten metal.

(*b*) **Displacement by means of sodium at a red heat.**—The chlorides of beryllium, magnesium, calcium, strontium, barium, aluminium, scandium, yttrium, lanthanum, ytterbium, cerium, thorium, vanadium, niobium, and tantalum are all reduced when added to sodium kept melted in an iron crucible. For boron, silicon, and titanium the double fluoride is more convenient, for the chlorides are volatile liquids. The process for manufacturing magnesium, which is carried out on a large scale, may be more minutely described as an example. The double chloride of magnesium and potassium, $MgCl_2.KCl$, carefully dried, is mixed with sodium in proportion to unite with the chlorine of the $MgCl_2$, the sodium being in small lumps. The iron crucible containing the mixture is heated; a violent reaction takes place, and magnesium is liberated:

$MgCl_2.KCl + 2Na = Mg + 2NaCl + KCl$. As magnesium is volatile, and can be distilled, it is purified by this operation. The contents of the crucible are treated with water; the potassium and sodium chlorides dissolve, and the globules of magnesium are collected, dried, and placed in a crucible, through the bottom of which a tube is fixed reaching nearly to the lid, and projecting some distance below the bottom. This crucible is placed in a furnace, and on raising the temperature, the magnesium volatilises up, passes down the tube, and the vapour condenses in the cooler part of the tube which projects below the furnace. This particular method of distillation is called *destillatio per descensum*. The other elements mentioned are too little volatile to admit of purification by this means. In their case, the cooled mass is treated with alcohol in order to remove the excess of sodium, and then with water to dissolve the resulting salt; the element is left in the state of powder.

(*c*) **Displacement by means of magnesium at a red heat.**—This process is sometimes used to prepare the element from its oxide. A mixture is made of magnesium filings with the oxide of the element, and it is heated in an iron crucible. The resulting mass is then treated with hydrochloric acid to remove the oxide of magnesium, which is thus converted into the soluble chloride. It is, of course, essential that the liberated element shall not be attacked by hydrochloric acid. The process works for the preparation of boron, silicon, and titanium.

(*d*) **Displacement by heating the oxide with carbon.**—This process is of the most general application. If the element is volatile, it is distilled from an iron or fire-clay retort; in this way sodium, potassium, rubidium, arsenic, zinc, and cadmium are prepared. If non-volatile at a red heat, a mixture of the oxide with charcoal is heated to bright redness in a clay crucible. On a manufacturing scale, coal or coke is substituted for the charcoal. The process is applicable to the production of indium, thallium, germanium, tin, lead, manganese, iron, cobalt, nickel, and copper. To exemplify this method, four instances will be described—the preparation of phosphorus, sodium, zinc, and iron.

Phosphorus.—The commonest natural compounds of phosphorus are phosphorite or calcium phosphate, $Ca_3(PO_4)_2$, and gibbsite or aluminium phosphate, $AlPO_4$. It is accordingly convenient and economical to prepare phosphorus from one of them. The process depends on the displacing action of carbon on the oxide at a high temperature. There are two methods of effecting this. The first is: the phosphorite is mixed with dilute sulphuric acid; the hydrogen of the sulphuric acid replaces the calcium of the calcium phosphate: $Ca_3(PO_4)_2 + 3H_2SO_4.Aq = 3CaSO_4 + 2H_3PO_4.Aq$. Coke or charcoal is impregnated with the phosphoric acid and heated to redness, when the phosphoric acid loses water: $H_3PO_4 = HPO_3 + H_2O$. The mixture of metaphosphoric acid, HPO_3, with carbon is charged into retorts of Stourbridge clay, the mouths of which are attached to a vertical copper tube, the lower end of which dips under water. On raising the retorts to a white heat, phosphorus distils over and condenses in the water. The final equation is: $4HPO_3 + 12C = 2H_2 + P_4 + 12CO$. By the second method, the calcium and aluminium phosphates are mixed with silica and carbon, and distilled from an electric furnace heated to whiteness by an arc in its interior.

Sodium.—A mixture is made of "spongy iron" (see p. 19) and pitch. This mixture is heated to redness in order to decompose the pitch, which consists of compounds of carbon and hydrogen. These compounds are decomposed, and a part of the carbon is left mixed with the spongy iron, while the hydrogen escapes in combination with the rest of the carbon. To this mixture, placed in an iron crucible, caustic soda is added; the lid of the crucible, which is furnished with a curved tube sloping downwards to a condenser, is fixed in place, and the crucible is heated in a furnace to bright redness. The carbon removes oxygen both from the hydrogen and the sodium, and sodium and hydrogen pass over into the condenser along with carbon monoxide, the sodium alone condensing, for the others are gaseous and escape. The equation is: $2NaOH + 2C = 2CO + H_2 + 2Na$. The condenser consists of a flat hollow copper vessel; the sodium is raked out as it accumulates.

Zinc.—The chief ore of zinc is the sulphide. To convert it into the oxide, it is roasted on a flat hearth in a current of air: $2ZnS + 3O_2 = 2ZnO + 2SO_2$. The oxide is mixed with small coal (slack) and placed in cylindrical retorts of fireclay. These retorts have pipes of rolled sheet-iron luted to the open ends with fireclay; they are packed into a furnace in tiers, and the temperature is raised to bright redness. The coal distils first, giving off coal-gas, which expels air from the retorts. When the temperature exceeds 1000°, the zinc distils and condenses in the iron pipes. It happens that almost all zinc ores contain cadmium sulphide, which, like zinc sulphide, is converted into oxide by roasting; and on distillation, the cadmium, which is the more volatile metal, distils over first and condenses in the outer portion of the tubes. These are untwisted and the metal removed with a chisel.

Iron.—The chief ores of iron are the carbonate and the oxide. The former is practically always mixed with clay (clayband) or with coal (blackband), and generally contains sulphur and phosphorus in the form of calcium sulphate, $CaSO_4$, and calcium phosphate, $Ca_3(PO_4)_2$. The sulphur is sometimes present in the form of iron pyrites, FeS_2. The ore is roasted to expel carbon dioxide, thus: $4FeCO_3 + O_2 = 2Fe_2O_3 + 4CO_2$. If it were then in its impure state smelted with coal, the iron would not flow, but would remain mixed with the clay. However, this process, if the ore is pure and charcoal is used as fuel, yields a mass of iron sponge, which can be heated and welded by hammering into a coherent mass.

The process is still used by Africans, and was at one time universal. On the large scale, however, it is necessary to add lime in order to form a flux with the clay. Clay consists of a compound of silica, SiO_2, and alumina, Al_2O_3, and with lime it melts to a glassy slag. Alternate layers of coal, lime, and the roasted ore are fed in at the top of a blast-furnace, a tall conical erection of firebrick, strengthened by being bound with iron hoops; at the bottom there is a "crucible," or receptacle for the molten iron, which can be discharged when required by forcing a hole in its side with an iron bar. There are also holes which admit water-jacketed tubes or "tuyères," which convey a blast of air heated to about 600° to increase the temperature of combustion of the coal. Here the reduction takes place in the upper part of the furnace, owing to the carbon monoxide formed by the combustion of the coal in the lower part of the heated mass; it acts on the oxide of iron thus: $Fe_2O_3 + 3CO = 2Fe + 3CO_2$. As the iron passes down the furnace it melts, and is met by the fused slag; it then coheres and runs into the crucible, whence it is drawn off from time to time.

Carbon unites with molten iron, forming a carbide; hence the product of the blast-furnace is not pure iron, but a mixture of iron with its carbide, and also with its sulphide and phosphide, if the ore has contained sulphates or phosphates. When such impure iron is brought in contact with oxygen in a molten or semi-molten condition, the carbon, sulphur, and phosphorus are oxidised mostly before the iron. If lime be present, sulphate and phosphate of calcium are formed. The modern process of removing these impurities is to pour the molten metal into a pear-shaped iron vessel lined with bricks made of magnesia; while it is molten, air is blown through the metal, and the carbon burns to carbon dioxide; the sulphur and phosphorus are likewise oxidised and combine with lime, a layer of which floats on the surface of the molten metal. When these impurities have thus been removed in the "Bessemer converter," the metal is poured into a mould. Steel is a mixture of iron with a trace of its carbide, and it is produced by mixing with the blown iron, before it is poured, a quantity of iron containing carbon and manganese (a metal which confers valuable properties on iron). The quantity of carbon in steel may vary between 0.6 and 1.5 per cent.; with the content of carbon varies also the quality of the steel; that with a small proportion is soft, with a high proportion hard.

(*e*) **Displacement by means of Oxygen.**—**Oxygen** is used in **Deacon's process** to liberate chlorine from hydrogen chloride. The latter gas, mixed with air, is passed through a chamber kept between the limits of temperature 375°–400°, containing bricks soaked with cupric chloride, $CuCl_2$. At this temperature the cupric chloride decomposes into cuprous chloride, $CuCl$, and free chlorine, but the cuprous chloride is reconverted into cupric chloride at the expense of the chlorine produced by the interaction of the hydrogen chloride and the air, thus: $4HCl + O_2 = 2H_2O + 2Cl_2$. The cupric chloride is again decomposed. This kind of action, where a limited quantity of a substance, itself not permanently changed, causes an apparently unlimited change in other reacting bodies, is termed "surface action," for its rate is dependent on the extent of the surface of the agent; and the name "catalysis" is sometimes given to such an action. The action would take place independently of the catalytic agent, but at a very slow rate; the presence of the catalyser has the effect of greatly increasing the rate at which the change takes place. The chlorine thus prepared is not pure, but mixed with the nitrogen and argon of the air, but it serves for some purposes. The rate of such action of oxygen in displacing bromine or iodine from their compounds with hydrogen is much greater, and at a high temperature the elements could be formed thus, but they are not usually produced in this way.

The preparation of **nitrogen** may be also regarded as a displacement by means of oxygen. Ammonia burns in oxygen, thus: $3NH_3 + 3O_2 = 3H_2O + N_2$, but at the same time some of the nitrogen unites with the oxygen and forms NO_2, nitric peroxide: this gas interacts with the ammonia, forming ammonium nitrate and nitrite, NH_4NO_3 and NH_4NO_2. If, however, the oxygen be not free, but in combination with an easily reduced metal, such as copper, it will combine with the hydrogen of the ammonia at a red heat, setting free the nitrogen. Another method involves the mutual displacement of nitrogen from its oxide by means of hydrogen, and from its hydride, ammonia, by oxygen: $2NH_3 + N_2O_3 = 3H_2O + 2N_2$. This method is, however, usually represented by the equation $NH_4NO_2 = 2H_2O + N_2$; for ammonium nitrite, NH_4NO_2, may be regarded as a compound of N_2O_3 with $2NH_3$ and H_2O. To obtain nitrogen by this method, since ammonium nitrite is not easily obtained, a solution of ammonium chloride may be warmed with one of sodium nitrite. The equation is then: $NaNO_2.Aq + NH_4Cl.Aq = 2H_2O + N_2 + NaCl.Aq$. Another convenient method is to warm together solutions of sodium hypobromite and ammonium chloride; the former loses oxygen readily, which combines with the hydrogen of the ammonia according to the equation: $3NaOBr.Aq. + 2NH_4Cl.Aq. = 3NaBr.Aq. + 3H_2O + 2HCl.Aq. + N_2$.

Although sulphur, selenium, and tellurium burn in oxygen, still they may be displaced from their hydrides, H_2S, H_2Se, and H_2Te, by means of oxygen at a red heat, provided the oxygen is present only in sufficient quantity to combine with the hydrogen, thus: $2H_2S + O_2 = 2H_2O + S_2$. Aqueous solutions of these compounds, too, are decomposed on standing, in contact with air, owing to similar displacement. Oxygen may displace mercury from its sulphide, cinnabar, HgS, which is the common ore of mercury; here the sulphide is roasted in air, when the sulphur combines with the oxygen to form sulphur dioxide, a gas at ordinary temperature; and mercury is liberated, also in the gaseous form, but condensing at temperatures below 358°.

(*f*) **Displacement by use of Fluorine, Chlorine, and Bromine.—Fluorine, chlorine,** and **bromine** may also be employed as displacing agents for nitrogen and oxygen.

A current of fluorine led through water displaces the oxygen, forming hydrogen fluoride; but the oxygen is in an allotropic state (see Part i.), called "ozone." Again, if a stream of chlorine is passed through, or if bromine-water be added to, a solution of ammonia, the hydrogen and chlorine combine, while the nitrogen is set free: $2NH_3.Aq + 3Cl_2 = 6HCl + N_2$; but as ammonia combines with hydrogen chloride, the reaction $6NH_3 + 6HCl = 6NH_4Cl$ occurs simultaneously; the complete equation is the sum of these two: $8NH_3.Aq + 3Cl_2 = 6NH_4Cl.Aq + N_2$.

Chlorine, added to a solution of bromide or iodide of a metal, displaces the bromine or iodine; here the non-ionised chlorine becomes ionised at the expense of the charge on the ionised bromine or iodine, while the latter lose their charges, thus: $2\overset{+}{K}\overset{-}{Br}.Aq + Cl_2.Aq. = 2\overset{+}{K}\overset{-}{Cl}.Aq + Br_2.Aq$. Similarly, bromine displaces iodine from a soluble iodide. But iodine displaces chlorine from the nearly insoluble silver chloride. Here, the iodine is still less soluble than the chloride; and as chloride dissolves, the less soluble and therefore non-ionised iodide is formed.

(*g*) Many metals are able to displace others. Thus, **iron** placed in a solution of a copper salt displaces the copper; **copper** displaces silver; **silver,** gold. In all these cases the action is doubtless an electrical one, and dependent on the replacement of a metal of lower by one of higher electric potential; that of higher potential becomes ionised, while that of lower assumes the metallic state, thus: $\overset{++}{Cu}\overset{-}{Cl_2}.Aq + Fe = \overset{++}{Fe}\overset{-}{Cl_2}.Aq + Cu$; $2\overset{+}{Ag}\overset{-}{NO_3}.Aq + Cu = \overset{++}{Cu}(\overset{-}{NO_3})_2.Aq + 2Ag$.

(*b*) There are some plans of obtaining elements which, though they can be referred to one or other of the three general methods exemplified already, are, on account of their complexity, better treated separately. Among these are the methods of separating hydrogen. The metals of the alkalies and alkaline earths attack water, forming hydroxides and liberating hydrogen : $2Na + 2H_2O = 2NaOH + H_2$; $Ca + 2H_2O = Ca(OH)_2 + H_2$. Magnesium powder, boiled with water, gives off hydrogen slowly; but zinc requires the presence of an acid, and must not be pure, *i.e.* there must be a foreign metal present to serve as the anode. The impurity usually present in commercial zinc is lead; the acid, for instance, sulphuric acid, is present in dilute solution as ions of $\overset{+\ +}{HH}$ and $\overset{-\,-}{SO_4}$; the $\overset{-\,-}{SO_4}$ removes the surface layer of the zinc as $\overset{++}{Zn}$, while the negative charge is transferred to the lead, which is in metallic contact with the zinc. This charge is neutralised by the positive charge of the $\overset{+\ +}{HH}$, which, on being discharged, escapes in an non-ionised state. It may then be collected over water, in which it is very sparingly soluble. **Hydrogen,** while it is on the point of discharging and is still in the ionised state, may be used to liberate certain elements from their oxides or chlorides. Zinc and hydrochloric acid, for instance, in a solution of stannous chloride, $\overset{++-}{SnCl_2}.Aq$, causes a deposition of tin owing to the exchange of charge; the hydrogen retaining its charge instead of parting with it to the lead or other impurity in the zinc, while the tin is discharged in its stead. If zinc and hydrochloric acid are placed in contact with silver chloride, AgCl, which is an insoluble compound, the hydrogen remains charged, while the silver parts with the chlorine, the latter remaining in solution with negative charge. Lastly, if generated in a solution of ferric chloride, $\overset{+++\ -}{Fe\ Cl_3}.Aq$, the zinc goes into solution as before; and the positive electricity is provided by the loss of a positive charge provided by the ferric ions changing to the ferrous ions of ferrous chloride, $\overset{++}{Fe}\overset{-}{Cl_2}.Aq$, and another molecule of $\overset{+}{H}\overset{-}{Cl}.Aq$ exists in solution. The valency of the iron is lowered. Such processes are generally termed *reduction ;* the hydrogen is said to be in the "nascent state," and is named the "reducing agent."

Metallic **iron, manganese, cobalt,** and **nickel** at a red heat remove oxygen from water with liberation of hydrogen: $3Fe + 4H_2O = Fe_3O_4 + 3H_2$; $2Co + 2H_2O = CoO + O_2$. Conversely, a current of **hydrogen** passed over these oxides at a red heat will combine with their oxygen, reducing them to metal. This is an instance of mass-action. From the equations given above, it is seen that hydrogen is formed; it does not remain in the tube to re-form water; if it did, there would be a state of balance or equilibrium, all four substances remaining together in proportions depending on the temperature and on their nature; in the current of steam, however, the hydrogen is carried on, and is no longer present to act on the oxide of the metal. And in the converse action the hydrogen conveys the steam away, so that it can no longer be deprived of oxygen by the metal.

As already remarked, **carbon monoxide** has a similar reducing action on the oxides of the more easily reducible elements. The product in this case is the dioxide, CO_2, for example, $Fe_2O_3 + 3CO = 2Fe + 3CO_2$. This action requires a red heat. Another reducing agent, applied by fusing the oxide with it, is **potassium cyanide**, KCN; it is converted into the cyanate, KCNO. The metal thallium may be prepared by its help, $Tl_2O + KCN = 2Tl + KCNO$. As the cyanide is somewhat expensive, it is used only in special cases.

An instance has already been given of the mutual reduction of two compounds in the case of nitrogen. Similar instances are known with lead and with sulphur. The chief ore of lead is the sulphide, a natural product termed *galena.* It is roasted, *i.e.* heated in contact with air to a red heat. After a portion has been oxidised to sulphate, $PbS + 2O_2 = PbSO_4$, the temperature is raised, when the sulphide and the sulphate mutually reduce each other: $PbS + PbSO_4 = 2Pb + 2SO_2$. With sulphur the partial burning of sulphuretted hydrogen may be explained in a similar manner; the reaction, $2H_2S + O_2 = 2H_2O + S_2$, may be represented as the formation of water and sulphur dioxide by the complete combustion of one-half of the hydrogen sulphide, and its reaction with the remaining sulphide, thus: $2H_2S + SO_2 = 2H_2O + 3S$. And, as a matter of fact, that reaction does take place on mixing the two gases in the required proportion of two volumes of hydrogen sulphide with one of sulphur dioxide.

The Properties of the Elements.—It has been customary to divide the elements into two classes, the metals and the non-metals. As we have seen, this classification is a completely arbitrary one; for there are some elements capable of existing in both states. The name "metal" was originally given to seven substances, all alike in possessing that bright lustre known as "metallic." These were gold, silver, mercury, copper, iron, lead, and tin. But in the Middle Ages bismuth and antimony were isolated in a fairly pure state, and these, together with zinc, were at first not received into the class, but were regarded as spurious; for they were brittle and easily oxidisable. Although there is no reason for retaining the division, yet it is often convenient. Bodies which possess metallic lustre have the power of conducting electricity better than transparent bodies, and they are also relatively good conductors of heat.

The elements exist in various physical states. Those which are gases at the ordinary temperature, however, have all been condensed to the liquid state by sufficient reduction of temperature. The lowering of temperature is most easily produced by means of liquid air, now a cheap commodity. To liquefy air, it is compressed by a pump to a pressure of 150 atmospheres; it then traverses a coil of copper pipe, and escapes from an orifice at the lower end. Now, compressed air has some resemblance to a liquid, for when it expands, as when a liquid changes to gas, heat is absorbed. The rapidly escaping air becomes cold, and in passing up over the coil of tube through which it has descended, it cools the pipe, so that the air passing down becomes colder and colder; finally, it is so cooled that it liquefies, and escapes from the orifice in a liquid state. It may be poured from one vessel to another, with little loss by evaporation; and if other gases be allowed to stream into a tube cooled by its aid, they too are liquefied. The principle of liquefying hydrogen is the same, for its boiling-point lies so low that it cannot be liquefied by the aid of liquid air. That of helium is still lower, but it too has yielded when compressed into a tube cooled by liquid hydrogen.

The elements which are gases at the ordinary temperature are hydrogen, helium, neon, argon, krypton, xenon, nitrogen, oxygen and ozone, fluorine, and chlorine. The first seven are colourless, both in the gaseous and the liquid state. Oxygen is a colourless gas, but forms a pale blue liquid; gaseous ozone has a blue colour; fluorine is pale yellow; and chlorine has a greenish-yellow colour. It forms a white solid, which, however, melts to a bright green liquid. Bromine is a dark red liquid at atmospheric temperature, but above its boiling-point, 59°, it is a deep red gas. Iodine is a blue-black solid, melting to a black liquid at 114°, and giving off a violet vapour. Ozone and the "halogens," as fluorine, chlorine, bromine, and iodine are called, have all a powerful odour, and act on the skin in a corrosive manner. Chlorine and bromine are soluble in water.

Among the other non-metallic elements are boron, a black, dusty, infusible powder; carbon, in its ordinary form an amorphous (*i.e.* non-crystalline) black substance, of which the most familiar variety is charcoal; carbon does not fuse, but at the enormously high temperature of the electric arc it volatilises; silicon, a blackish-brown powder, melting at bright redness to a lustrous liquid, which solidifies in shining black lumps; phosphorus, a waxy, pale yellow solid, melting at 44.4°; sulphur and selenium, yellow and brown-red solids, the former melting at 115° to a brown liquid, and boiling at 446°; the latter forming a black liquid at 217°, and a black vapour at 665°.

The metals of the alkalies, as they are usually called, lithium, sodium, potassium, rubidium, and cæsium, are soft white metals, at once attacked by water, and oxidised readily by air, cæsium, indeed, taking fire spontaneously. To protect them from oxidation, they must be kept under rock-oil or ligroin, a compound which contains no oxygen. Of these, cæsium has the lowest and lithium the highest melting-point. The metals calcium, strontium, and barium are sometimes named the "metals of the alkaline earths." They are hard white bodies, also, like those of the sodium group, oxidising readily on exposure to air, and at once attacked by water. Magnesium, zinc, and cadmium are noteworthy, inasmuch as their temperature of ebullition is not so high that it cannot be reached in an ordinary furnace; they can therefore be distilled. Magnesium and zinc are hard and brittle; cadmium is softish, like lead, and of a somewhat greyer tint.

The remaining elements may be classed under the headings, "hard," "soft," "brittle," &c. This implies only their behaviour at ordinary temperatures; at higher or lower temperatures the properties are materially changed. Mercury, for example, below −40°, is malleable; lead is brittle.

(*a*) **Malleable metals :—**

(1) *White, ductile, moderately hard :*—beryllium, aluminium, gallium, indium, tin, silver, nickel. *Red*, copper. *Yellow*, gold.

(2) *Grey-white, ductile, and moderately hard :*—iron, manganese, cobalt.

(3) *Grey-white and soft; ductile:*—thallium, lead; *somewhat harder, and fusible only at a very high temperature:*—rhodium, ruthenium, palladium, platinum, iridium.

(*b*) *Liquid metal:*—mercury.

(*c*) **Brittle metals**:—

(1) *White, hard:*—antimony, bismuth, tellurium, zirconium, didymium (a mixture), osmium, germanium. *Less hard*, arsenic.

(2) *Grey, hard:*—lanthanum, cerium, yttrium, uranium.

(3) *Grey powders, acquiring metallic lustre under the burnisher:*—thorium, niobium, tungsten.

(4) *Black powders:*—tantalum, titanium.

The elements scandium, samarium, and gadolinium have not been prepared.

Although the external properties of the elements does not show any obvious relation to their order in the periodic table (see Part I.), yet it may be generally remarked that the density increases as each column is descended. Among the lightest of the elements are lithium, beryllium, magnesium, and aluminium, at least in the solid state; whereas osmium, iridium, platinum, and gold are among the heaviest. But much more must be ascertained regarding their properties before a satisfactory comparison can be made.

CHAPTER II

Classification of Compounds—The Hydrides.

Classification of Compounds.—Compounds of the elements may be divided conveniently into six classes:—

The **Hydrides**;
The **Halides**;
The **Oxides** and **Sulphides** (with **Selenides** and **Tellurides**);
The **Nitrides** and **Phosphides** (with **Arsenides** and **Antimonides**);
The **Borides, Carbides,** and **Silicides**;
The **Alloys.**

Compounds can be prepared by many methods; it is not so easy to classify them as it is to arrange into classes the methods of preparation of elements. As a rule, the preparation is carried out by one of the following methods:—

(*a*) **The interaction of elements;**
(*b*) **The action of an element on a compound;**
(*c*) **The action of heat on a compound;**
(*d*) **The interaction of compounds;**
(*e*) **The addition of one compound to another.**

These methods shall be considered in relation to each of the groups of compounds named above.

The Hydrides.

(*a*) **The Interaction of Elements.—Lithium, sodium,** and **potassium,** when heated to 300° in an iron tube in a current of hydrogen, form white waxy compounds; that of lithium has the formula **LiH**; as the sodium compound has the formula Na_2H, its existence is difficult to reconcile with the usual valency of either hydrogen or sodium, for these elements in all other compounds behave as monads. It would repay further investigation. It decomposes at 421°.

Iron, nickel, palladium, and **platinum,** when heated gently in hydrogen, absorb the gas. Meteoric iron, indeed, has been known to give off, on heating, 2.85 times its volume of gas. This natural variety of iron contains about 6 per cent. of nickel. Palladium, gently warmed in an atmosphere of hydrogen, absorbs over 900 times its volume of that gas, corresponding to 4.68 per cent. of the weight of the body produced. It is difficult to determine whether or not the palladium is in chemical combination with the hydrogen, or whether the hydrogen is in a state analogous to solution, for it is known that a solid can exert solvent power. There is a considerable rise of temperature accompanying the absorption; and if palladium, in a state of sponge, is placed in contact with a mixture of oxygen and hydrogen, the mixture may be made to explode. A thermometer-bulb coated with palladium sponge is a good test for the presence of an explosive mixture of marsh-gas and air in mines, for the rise of temperature produced is an indication of danger. These metals absorb hydrogen more readily if they are made the negative electrodes of a battery with which dilute sulphuric acid is electrolysed. Iron shows a very curious behaviour under these circumstances. If a thin plate of iron is made to close the top of a barometer-tube full of mercury and a small cell be constructed on it, hydrogen will pass through the iron, when the plate is made the kathode, and will depress the mercury in the tube. No other metal, so far as is known, shows this peculiarity; it would appear that the hydrogen in the ionic state can penetrate the iron.

Carbon, heated to 1200° in an atmosphere of hydrogen, unites with it to form **marsh-gas (methane), CH_4**. Only a small percentage of the hydrogen, however, enters into combination ; a balance soon establishes itself between the number of molecules of methane being formed and decomposed in unit time. At a higher temperature, that of the electric arc, **acetylene, C_2H_2,** is formed, owing to the decomposition of the methane into that gas and free hydrogen :—$2CH_4 = C_2H_2 + 3H_2$. Other compounds of carbon and hydrogen are formed simultaneously, and there again appears to be a state of equilibrium produced between the various hydrocarbons formed. With **nitrogen, NH_3,** it appears to be impossible to induce hydrogen to enter into direct combination at such temperatures ; but if electric sparks be passed through a mixture of hydrogen and nitrogen, combination to a limited extent ensues. Should the ammonia, NH_3, be removed by having water, or, better, dilute sulphuric acid, present, the combination proceeds until all the gases, if they were originally present in the correct proportion—one volume of nitrogen to two volumes of hydrogen—have combined. Conversely, if sparks be passed through ammonia gas, there is nearly, but not quite, complete decomposition into its constituents. This enables the volume relations of ammonia to be demonstrated ; for it is found that two volumes of ammonia gas can be decomposed into two volumes of nitrogen and six volumes of hydrogen. This is symbolised by the equation—

$$\begin{array}{llll} & 2NH_3 = & N_2 \;+ & 3H_2 \\ \text{Weight} & 2(14+3) & 28 & 3(2)\ \text{grams.} \\ \text{Volume} & 2(22.4) & 22.4 & 3(22.4)\ \text{litres.} \end{array}$$

The hydrogen can be nearly completely removed by absorption with palladium-sponge, and the nitrogen remains.

Water, H_2O, is more completely formed than any one of the previously mentioned compounds by the interaction of its elements. A mixture of oxygen and hydrogen, in the proportion of one volume of oxygen to two of hydrogen, is exploded by heat ; this is most easily done by passing an electric spark through the mixture. While the position of equilibrium for a mixture of nitrogen, hydrogen, and ammonia lies at such a point that very little of the compound is present, but chiefly the uncombined gases, the contrary is the case with hydrogen and oxygen. Here nearly all the oxygen and hydrogen combine, and only a trace remains uncombined. Combination may be made to take place slowly at much lower temperatures; even at 300° slow combination occurs. Colloidal platinum, prepared by making an electric arc between poles of platinum under pure water, which appears to consist of very finely divided platinum disseminated through the water, has the power of causing union of oxygen and hydrogen left standing in contact with it, even at the temperature of the atmosphere. On the other hand, if water-vapour be raised to a very high temperature, above 1800°, decomposition into its constituents takes place with considerable rapidity; so that it is possible to obtain a mixture of oxygen and hydrogen by passing steam through a tube in which a spiral of platinum wire is kept at a white heat by means of an electric current. These actions are therefore termed "reversible," and they are expressed by such equations as—

$$CH_4 \rightleftarrows C + 2H_2 ; \qquad 2H_2 + O_2 \rightleftarrows 2H_2O ;$$
$$N_2 + 3H_2 \rightleftarrows 2NH_3.$$

Hydrogen also combines with **sulphur** when passed through a flask containing boiling sulphur, and sulphuretted hydrogen, $\mathbf{H_2S}$, decomposes when raised to a low red heat.

Interesting relations are to be seen with the compounds of the **halogens** with hydrogen. In preparing fluorine by the electrolysis of hydrogen-potassium fluoride, KHF, in presence of hydrogen fluoride, H_2F_2, it is possible, by stopping the exit of the hydrogen, to cause a bubble to pass the bend of the U-tube and to rise into the fluorine; the instant the gases unite there is a sharp explosion. This shows that these gases unite even in the dark to form $\mathbf{H_2F_2}$. Chlorine and hydrogen, on the other hand, do not combine in the dark, but, when exposed to diffused daylight, slow but complete combination ensues ; in bright sunlight, or when illumined by the light from burning magnesium, the mixture of gases explodes, forming **HCl**. Bromine and hydrogen unite to form **HBr** when a current of hydrogen, having bubbled through a wash-bottle of bromine, passes through a red-hot tube ; with excess of hydrogen the union is practically complete. Iodine and hydrogen, on the contrary, unite very incompletely to produce **HI** ; and if hydrogen iodide be heated, a large proportion of it is decomposed into hydrogen and iodine. This change has been investigated much more completely than other changes of the same character already mentioned ; and as it is characteristic of all such reversible reactions, we shall consider it in somewhat greater detail.

The rate at which hydrogen iodide is produced from a mixture of hydrogen and iodine at any constant temperature is much more rapid than that at which the reverse change of hydrogen iodide into iodine and hydrogen takes place. This rate was not difficult to determine. Weighed quantities of iodine were placed in a tube filled with hydrogen, and after heating the sealed tube for a sufficiently long time for equilibrium to be established, it was opened under water. The hydrogen iodide formed at once dissolved in the water, and the residual hydrogen was measured. The amount of uncombined iodine remaining in the water was then estimated by known processes. It was thus possible to find the ratio of the combined to the uncombined hydrogen. Now, it was discovered many years ago that the rate of chemical change depends on the amount of each of the reacting substances present in unit volume—a condition expressed by the term "active mass." Thus, if we double the amount of hydrogen in the mixture of the gases mentioned, we double its "active mass." Let i_2 denote the number of molecules in unit volume of the iodine gas, and h_2 that of the hydrogen, and let $2hi$ be that of the hydrogen iodide formed by their interaction. Then, as the rate of formation of hydrogen iodide is proportional both to i and to h, it will be proportional to their product, $h \times i$. And as $H_2 + I_2 = 2HI$, the rate of change of HI into H_2 and I_2 will be $2hi \times 2hi$ or $4(hi)^2$. If we call the rate of formation k, and that of decomposition k', the proportion of these rates to each other will be $k/k' = (h \times i)/4(hi)^2$, if the gases are present in molecular proportions. At the temperature 440°, and at one atmosphere pressure, it was found that, taking the total hydrogen as unity, 0.28 was free and 0.72 combined, after a sufficient time had been allowed for the change to complete itself. Now, the iodine free must have been equal in number of molecules to the free hydrogen, *i.e.* 0.28, and the same number of atoms of iodine must have existed in combination as of hydrogen in combination; hence $0.28 \times 0.28/4(0.72 \times 0.72) = 0.0375 = k/k'$. This means that at 440° molecules of hydrogen iodide decompose into hydrogen and iodine at a rate only 0.0375 (or one twenty-sixth) of that at which combination takes place between the two gases.

(*b*) **The action of an element on a compound** leads to the formation of many hydrides. This process has been pretty fully treated in the description of the methods of preparation of elements. For example, on passing a current of hydrogen over hot cupric oxide, water, $\mathbf{H_2O}$, is formed, while the oxide is reduced to copper, $CuO + H_2 = Cu + H_2O$. The oxides mentioned on p. 16 are thus reduced. It is not so usual for sulphides to lose sulphur on heating them in a stream of hydrogen; indeed, it is only those sulphides which themselves decompose when heated that yield to such treatment; but hydrogen fluoride, chloride, bromide, and iodide are formed on heating the halides of many metals in a current of hydrogen. The process, however, is not one which is used for the preparation of these hydrides.

(*c*) The third method—that of **heating a compound**—is also not in use as a means of preparing hydrides, but it is often employed in order to produce the compound from which the hydride is separated. Thus, all compounds containing water of crystallisation, when heated, lose water when raised to a high temperature; and double compounds of ammonia, too, lose ammonia on rise of temperature. Such compounds as calcium chloride, $CaCl_2$, crystallise with water. The formula of the hydrated compound is $CaCl_2.6H_2O$; a similar compound with ammonia, $CaCl_2.6NH_3$, is also known; compounds like these lose water or ammonia when heated. By this plan **Faraday** succeeded in liquefying ammonia, which at ordinary temperatures is a gas. Having sealed up the ammonio-chloride of calcium or of silver, $AgCl.NH_3$, in an inverted U-tube, one leg was cooled with a freezing mixture, while the other was heated, and the gas liquefied under the combined influence of cold and pressure.

(*d*) Most of the hydrides can be prepared by the fourth method—**the interaction of compounds.** The decomposing agent is either water, an acid, or an alkali.

(1) Water:—Marsh-gas, $\mathbf{CH_4}$, ethylene, $\mathbf{C_2H_4}$, acetylene, $\mathbf{C_2H_2}$, ammonia, $\mathbf{NH_3}$, and phosphoretted hydrogen, $\mathbf{PH_3}$, may be produced by the action of water on some compounds of carbon, nitrogen, and phosphorus. Aluminium carbide, Al_4C_3, yellow transparent crystals produced by heating a mixture of carbon and oxide of aluminium to whiteness in the electric furnace, on treatment with water yields pure methane, $Al_4C_3 + 12H_2O = 3CH_4 + 4Al(OH)_3$. Manganese carbide, black crystals produced by heating in the electric furnace a mixture of manganese oxide and carbon, yields a mixture of equal volumes of hydrogen and methane, $Mn_3C + 6H_2O = 3Mn(OH)_2 + CH_4 + H_2$. Lithium, calcium, strontium, and barium carbides also formed in a similar manner in the electric furnace yield acetylene with water, $Li_2C_2 + 2H_2O = 2LiOH + C_2H_2$; $CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$. The carbides of cerium, CeC_2, lanthanum, LaC_2, yttrium, YC_2, and thorium, ThC_2, yield a mixture of methane, ethylene, C_2H_4, and acetylene, sometimes mixed with hydrogen;

and uranium carbide, U_2C_2, gives methane, ethylene, and hydrogen, but no acetylene.

Magnesium or calcium nitrides, prepared by heating metallic magnesium or calcium in a current of nitrogen, yield ammonia with water: $Mg_3N_2 + 6H_2O = 2NH_3 + 3Mg(OH)_2$, and calcium phosphide, produced by heating lime with phosphorus, on treatment with water similarly gives off phosphoretted hydrogen: $Ca_3P_2 + 6H_2O = 3Ca(OH)_2 + 2PH_3$. The sulphides of magnesium and aluminium, MgS and Al_2S_3, are also decomposed by water, with production of hydrogen sulphide and the hydroxide of the metal: $MgS + 2H.OH = Mg(OH)_2 + H_2S$; $Al_2S_3 + 6H.OH = 2Al(OH)_6 + 3H_2S$.

The halides of a certain number of elements are at once decomposed by water with formation of a hydride of the halogen and a hydroxide of the element. Boron, silicon, titanium, phosphorus, sulphur, selenium, and tellurium chlorides, bromides, and iodides are thus resolved. The method is practically made use of in preparing hydrogen bromide, **HBr**, and iodide, **HI**, by help of phosphorus. But the previous preparation of phosphorus bromide or iodide is unnecessary. It is sufficient to add bromine to water in contact with red phosphorus, and hydrogen bromide is evolved; or to warm a mixture of iodine, water, and red phosphorus. The use of yellow phosphorus is not advisable, for the action is apt to take place too violently if it be used. It may be supposed that the phosphorus and halogen unite to form the pentahalide, which is then immediately decomposed by the water, thus: $PBr_5(\text{or } PI_5) + 4H_2O = H_3PO_4 + 5HBr(\text{or } 5HI)$. The gaseous hydride may be collected over mercury or by downward displacement, or it may be dissolved in water and a solution of hydrobromic or hydriodic acid prepared.

A commercial method of producing hydrogen chloride, **HCl**, depending on the decomposition of magnesium chloride when heated in a current of steam, has been patented; it results in the formation of a compound of oxide and chloride of magnesium, while the hydrogen of the water unites with a part of the chlorine; the resulting gaseous hydrogen chloride is passed up towers, and comes into contact with water, thus yielding a solution of hydrochloric acid.

(2) In many cases the compound from which the hydride is formed is not decomposed by water; an acid, generally hydrochloric acid, must be present. The reason of this is not easily explained; it may be that the very few ions of $\overset{+}{\mathrm{H}}$ and $\overset{-}{\mathrm{O}}\mathrm{H}$ present in water are sufficient to effect the decomposition in some cases and not in others, and that when an acid is necessary the much larger number of ions of hydrogen present in its solution is required; also it is known that the heat evolved during the decomposition of those compounds which are altered by water is greater than that which would be evolved by those which resist its action were they to be attacked by water. Many hydrides are prepared by the help of acids. Magnesium boride, Mg_3B_2, yields with hydrochloric acid a trace of $\mathbf{BH_3}$; but as this compound is a very unstable gas, almost all of it decomposes into boron and hydrogen. The similar compound, Mg_2Si, produced by heating a mixture of silica and magnesium powder to redness, when mixed with hydrochloric acid yields hydride of silicon, $\mathbf{SiH_4}$, as a colourless, spontaneously inflammable gas:—$Mg_2Si + 4HCl.Aq = 2MgCl_2Aq + SiH_4$. Arseniuretted hydrogen, $\mathbf{AsH_3}$, and antimoniuretted hydrogen, $\mathbf{SbH_3}$, are prepared from sodium or zinc arsenide or antimonide: $Na_3As + 3HCl.Aq = 3NaCl.Aq + AsH_3$; $Zn_3Sb_2 + 6HCl.Aq = 3ZnCl_2.Aq + 2SbH_3$. These gases, however, may be obtained mixed with hydrogen if a solution of oxide of arsenic or antimony in hydrochloric acid, which yields chloride of arsenic or antimony, is treated with zinc. The first change is the replacement of the zinc by the arsenic or antimony, thus: $2\overset{+++}{\mathrm{As}}\overset{-}{\mathrm{Cl}}_3.Aq + 3Zn = 3\overset{++}{\mathrm{Zn}}\overset{-}{\mathrm{Cl}}_2Aq + 2As$. Electrically

neutral zinc replaces positively charged arsenic, itself becoming positively charged. The arsenic and the unattacked zinc form a couple, and the hydrochloric acid is electrolysed, $2\overset{+}{H}\overset{-}{Cl}.Aq + \overset{++}{Zn} = \overset{++}{Zn}\overset{-}{Cl_2}.Aq + 2\overset{+}{H}$; the hydrogen ion unites with the arsenic, negatively charged in the electric couple, forming electrically neutral hydride of arsenic, which escapes as gas, $3\overset{+}{H} + \overset{---}{As} = AsH_3$. An element in this form, capable of combination at the moment of liberation, is said to be in the nascent state, a word derived from "nascere," to be born. It differs from an ordinary element in being on the point of losing an electric charge, and it may either be evolved in the free state by combining with itself, as $\overset{+}{H} + \overset{+}{H} = H_2$, on giving up its charge, or it may enter into some other form of combination, as in the case explained. This process of preparing arsenic or antimony hydride is used as a test for the elements arsensic or antimony. It was devised by **Marsh**, and as the hydrides are very easily decomposed by a high temperature, the gas, if caused to pass through a red-hot tube, is decomposed, giving a deposit of arsenic (grey) or antimony (black). The former is more easily oxidised than the latter, and dissolves in a solution of bleaching-powder, in which the latter is insoluble. This process is particularly applicable where poisoning with arsenic or antimony is suspected.

H_2S, H_2Se, H_2Te.—Hydrogen sulphide, selenide, and telluride are prepared by treating a sulphide, selenide, or telluride with dilute sulphuric or hydrochloric acid: $FeS + \overset{+}{H_2}\overset{--}{SO_4}.Aq = \overset{++}{Fe}\overset{--}{SO_4}.Aq + H_2S$; $Sb_2S_3 + 6\overset{+}{H}\overset{-}{Cl}.Aq = 2\overset{+++}{Sb}\overset{-}{Cl_3}.Aq + 3H_2S$. $\overset{+}{Na_2}\overset{--}{Se}.Aq + \overset{+}{H_2}\overset{--}{SO_4}.Aq = \overset{+}{Na_2}\overset{--}{SO_4}.Aq + H_2Se$.

Acids.—Hydride of fluorine, chlorine, bromine, and iodine, when dissolved in water, are termed "acids." As already mentioned, this name was originally applied to compounds which possess a sharp taste and change the colour of certain vegetable colouring matters. The word was later extended to apply to compounds similar in function, although not acid to taste, which attack the carbonates, causing them to effervesce, and which yield salts with the oxides of metals. All acids contain hydrogen, and it is now possible to define them in a very simple manner. An acid, in fact, is a compound which yields hydrogen ions when dissolved in water, or in some other solvent capable of causing ionisation. This definition applies to the hydrides of fluorine, chlorine, bromine, and iodine; and also to those of sulphur, selenium, and tellurium; for on solution they ionise thus: $\overset{+}{H}\overset{-}{F}.Aq$; $\overset{+}{H}\overset{-}{Cl}.Aq$; $\overset{+}{H}\overset{-}{Br}.Aq$; $\overset{+}{H}\overset{-}{I}.Aq$; $\overset{+}{H}.\overset{-}{S}H.Aq$; $\overset{+}{H}.\overset{-}{Se}H.Aq$; $\overset{+}{H}.\overset{-}{Te}H.Aq$. But it is not confined to them, for the hydrogen may be united, not with a simple element, but with a complex group of elements, as in $\overset{+}{H_2}\overset{--}{SO_4}.Aq$ or $\overset{+}{H}\overset{-}{NO_3}.Aq$. Now, in dilute solution, a solution of sulphuric acid is less ionised than one of hydrochloric acid, in about the proportion of 1 : 2, and it is therefore a weaker acid; so that if a hydroxide, such as sodium hydroxide, be presented to a mixture of equal numbers of these molecules, in quantity requisite for only one of them, chloride of sodium will be formed in greater quantity than sodium sulphate; yet, on heating a halide with sulphuric acid, because hydrogen chloride is a volatile compound, it removes itself from the sphere of action in a non-ionised state while the sodium remains as sulphate. Hence these hydrides may be thus prepared. Hydrogen fluoride, $\mathbf{H_2F_2}$, is generally prepared by distilling calcium fluoride, a compound naturally occurring as "fluor-spar," with sulphuric acid in vessels of lead or platinum: $CaF_2 + H_2SO_4 = BaSO_4 + H_2F_2$. The use of lead or platinum is obligatory on account of the action of hydrogen fluoride on glass or porcelain, the materials of which flasks and retorts are usually made; for hydrogen fluoride attacks the silica which they contain, forming with it silicon fluoride: $SiO_2 + 2H_2F_2 = SiF_4 + 2H_2O$. Gold is almost the only other metal which resists the action of hydrogen fluoride. There is no such difficulty with the other halides. Hydrogen chloride, **HCl**, is prepared by distilling from a glass retort a mixture of common salt and oil of vitriol: $NaCl + H_2SO_4 = HNaSO_4 + HCl$. On a large scale this preparation is carried out in rotating circular furnaces, the mixture of salt and vitriol being delivered in through a hopper above, and at the high temperature the action goes further, and di-sodium sulphate is produced: $2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl$. The gas is passed up towers filled with coke, and exposed to a descending stream of water, in which it dissolves, forming a saturated solution of hydrochloric acid, or, as it used to be called, "muriatic acid" (from "muria," brine).

Hydrogen bromide, **HBr**, and iodide, **HI**, may similarly be produced by distilling together bromide or iodide of sodium or potassium with exactly the right weight of sulphuric acid for the equation $2KBr$ (or $2KI$) $+ H_2SO_4.Aq = K_2SO_4.Aq + 2HBr$ (or $2HI$). But in these cases, the hydrogen bromide or iodide is very apt to exert a reducing action on the sulphuric acid, depriving it of an atom of oxygen, thus:—$H_2SO_4 + 2HI = H_2SO_3 + H_2O + I_2$. Hence it is advisable to use phosphoric acid, H_3PO_4, a compound not thus reduced:—$H_3PO_4 + 2KI = HK_2PO_4 + 2HI$.

All these halides come over as gases, and may either be collected over mercury or by "downward displacement," *i.e.* by delivering them to the bottom of a jar containing air, which owing to its less density is forced upwards, and escapes at the mouth of the jar. They cannot be collected over water, for they are readily soluble in it.

The compound $\mathbf{HN_3}$, termed hydrazoic acid (from the French term for nitrogen, "azote"), is also liberated in the gaseous form by warming its sodium salt with sulphuric acid. It, too, is readily soluble in water.

(3) Certain hydrides are set free by the action of an

alkali, *i.e.* the hydroxide of one of the metals of the sodium or the calcium group. It is true that the change may be produced by other hydroxides, but they are not so efficient, and not so generally employed. Among these are ammonia, $\mathbf{NH_3}$, and hydrazine, $\mathbf{N_2H_4}$. These bodies unite with acids; for example, ammonia and hydrogen chloride form ammonium chloride, NH_4Cl, when mixed:—$NH_3 + HCl = NH_4Cl$. This compound is produced by a change in valency of the nitrogen atom; in ammonia it is a triad, N''', but on union with hydrogen chloride the valency of the nitrogen becomes five, N^v. On distillation of a mixture of ammonium chloride with caustic soda or with slaked lime, either in presence or absence of water, the following change occurs:—$NH_4Cl + NaOH = NaCl + NH_3 + H_2O$; $2NH_4Cl + Ca(OH)_2 = CaCl_2 + 2NH_3 + 2H_2O$. The initial change is the formation of ammonium hydroxide, NH_4OH; this substance, being unstable when heated, decomposes into ammonia and water. Hydrazine, a compound of the formula $\mathbf{N_2H_4}$, is similarly liberated from its chloride.

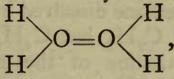
The usual source of commercial ammonia is coal-gas. On distillation of coal, all varieties of which contain nitrogen, it may be imagined that when methane, the principal constituent of coal-gas, is strongly heated it splits into carbon and hydrogen. This hydrogen, at the moment of its formation, is in the nascent state, and it unites with the nitrogen, which is also in the nascent condition. As ammonia is very easily soluble in water, while the other constituents of coal-gas are sparingly soluble, the gas is deprived of ammonia by passing it through "scrubbers," pipes containing broken bricks kept moist with water. The ammonia dissolves, while the coal-gas passes on. The solution is next mixed with hydrochloric acid and evaporated to dryness. The residue of ammonium chloride is then distilled with lime, as previously described. The ammonia is received in water, and brought into the market in the form of a concentrated solution, to which the name "liquor ammoniæ" is given.

(*b*) Certain double hydrides are formed by the addition of one hydride to another. Ammonia and hydrazine unite with hydrides of the halogens to form salts, such as ammonium chloride, NH_4Cl; but as these bodies show analogy with salts of the metals, they will be reserved until the latter are considered.

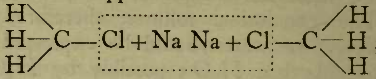
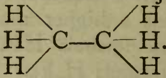
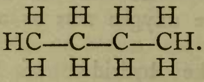
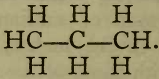
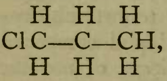
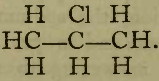
General Nature of the Hydrides.—Hydrides of **lithium, sodium, potassium, iron, nickel, palladium,** and **platinum** differ from the others in character; they are solid bodies, decomposed by heat. **Graham,** indeed, who investigated that of palladium, was struck with the metallic nature of the substance, and was inclined to believe that it might be regarded as an alloy of a metallic form of hydrogen, to which he gave the name "hydrogenium;" and it was for long believed that liquid hydrogen would show the characteristic property of metals, metallic lustre. But this anticipation has not been fulfilled. Liquid hydrogen is a colourless body; and solid hydrogen is described as having a white crystalline appearance, like ice froth. But it must be confessed that hydrogen shows a marked similarity to metals in many of its compounds, as will be frequently seen in the sequel.

The remaining hydrides may be divided into three classes:—Those which react with neither acid nor bases, and which may therefore be described as neutral. To this class belong the hydrides of **boron, carbon, silicon, arsenic,** and **antimony.** That of **phosphorus** nearly falls into the same category, for its compounds with acids are very unstable. The next class—those which react with bases—comprises water and the hydrides of **sulphur, selenium,** and **tellurium.** The compounds are termed hydroxides, or, in the case of sulphur, hydrosulphides. These will be considered later, but an instance may be given here:—When lime is moistened with water it is slaked, with formation of calcium hydroxide, thus: $CaO + H_2O = Ca(OH)_2$. The hydrides of **fluorine, chlorine, bromine,** and **iodine** also belong to this class; but in their case an exchange takes place, thus: $CuO + 2HCl.Aq = CuCl_2.Aq$

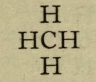
$= H_2O$. Hydrazoic acid is capable of similar reactions. Such hydrides, with the exception of water, are generally termed acids. The last group of hydrides, **ammonia** and **hydrazine**, and, in one or two isolated cases, hydrogen **phosphide**, unite with acids, forming salts, thus: $NH_3 + HCl = NH_4Cl$; $PH_3 + HI = PH_4I$. It appears that the presence of water is necessary for at least the first of these combinations; for if perfectly dry hydrogen chloride is mixed with perfectly dry ammonia, no combination results. It is perhaps allowable to suppose that the presence of moisture leads to ionisation of the hydrogen chloride, and that the ionised molecule is capable of entering into combination, while the non-ionised molecule is without action on the ammonia. These compounds will be treated of under the heading of "salts."

The hydrides of **boron**, **carbon**, **silicon**, **phosphorus**, **arsenic**, and **antimony** are insoluble in water; those of **nitrogen**, **sulphur**, **selenium**, **tellurium**, and the **halogens** are soluble. With the exception of certain hydrides of carbon, to be afterwards described, and water, all the rest are gases at atmospheric temperature. The fact that water is a liquid, and not, as might be expected, a gas, requires comment. It is noteworthy that water-gas possesses the density 9, corresponding to the molecular weight 18; hence there can be no doubt that in the gaseous state water has the formula H_2O. But it is known that compounds of sulphur, which are in formulæ, and in many properties analogous to compounds of oxygen, possess higher boiling-points than the corresponding oxygen compounds. For instance, bisulphide of carbon, CS_2, boils at 44°, whereas carbon dioxide boils at about –80°. But water boils at 100°, and, contrary to expectation, its analogue, sulphuretted hydrogen, condenses to a liquid at a temperature much below 0°. Now, it has been found by a method depending on the rise of liquids in capillary tubes, that while the molecular weight of most substances in the state of liquid is identical with those which they possess in the gaseous state, the molecular weight of water is considerably too great. The conclusion follows, therefore, that the molecular weight of water should be expressed by a more complex formula than H_2O; possibly by H_4O_2, or by one even more complex. Gaseous hydrogen fluoride, unlike its congeners, has a higher molecular weight than that expressed by the formula HF; determination of its density leads to the formula H_2F_2. These facts are probably to be explained by the view that oxygen may possess a higher valency than 2, and fluorine than 1, at relatively low temperatures. It is not unlikely that the structural formula of liquid water is , and that of hydrogen fluoride $HF{=}FH$, where oxygen acts as a tetrad and fluorine as a triad.

Hydrocarbons. — The hydrides of carbon, or "hydrocarbons," are very numerous, and form an important group of substances. In many respects they are analogous to the metals, and they yield derivatives comparable with those of the metals. The preparation of some of them has already been described; but in order to give a more complete idea of their structure and functions, a short description of other methods of forming them is annexed.

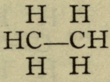
Methane or marsh-gas, if mixed with its own volume of chlorine, and exposed to daylight—not sunlight, else the mixture would explode—undergoes the reaction $CH_4 + Cl_2 = CH_3Cl + HCl$. The resulting gas, termed **chloromethane**, is soluble in ether, a volatile liquid compound of carbon, hydrogen, and oxygen. If pieces of metallic sodium are added to the solution, the sodium withdraws chlorine from the chloromethane and a gas is evolved. On analysis, it gives numbers answering to the formula CH_3. But if that were its formula, its molecular weight in grammes would occupy 22.4 litres; but 15 grammes occupy only 11.2 litres; hence its molecular weight must be 30, and not 15, and its formula cannot be CH_3, but must be C_2H_6. It is reasonable to suppose that the mechanism of the reaction is this: ; and that the two CH_3 groups on liberation join together, forming the complex group, . Similarly, mixing C_2H_6, which is named **ethane**, with its own volume of chlorine, a reaction takes place like that with methane, and **chlorethane** is formed, thus: $C_2H_6 + Cl_2 = C_2H_5Cl + HCl$. Chlorethane dissolved in ether and treated with sodium yields not C_2H_5 but C_4H_{10}, and it may be supposed that the constitution of the new hydrocarbon, **butane**, is  $\begin{array}{c}\text{H}\quad\text{H}\quad\text{H}\quad\text{H}\\ \text{HC—C—C—CH}\\ \text{H}\quad\text{H}\quad\text{H}\quad\text{H}\end{array}$. A mixture of chloromethane and chlorethane gives with sodium an intermediate hydrocarbon, C_3H_8, **propane**,  $\begin{array}{c}\text{H}\quad\text{H}\quad\text{H}\\ \text{HC—C—CH}\\ \text{H}\quad\text{H}\quad\text{H}\end{array}$. When chlorine and propane are mixed in equal volumes, two **chloropropanes** result; they have identical formulæ and molecular weights, and it is believed that the difference between them consists in the position of the entering atom of chlorine. In one case the chlorine replaces hydrogen attached to one of the terminal atoms of carbon, thus:  $\begin{array}{c}\text{H}\quad\text{H}\quad\text{H}\\ \text{Cl C—C—CH}\\ \text{H}\quad\text{H}\quad\text{H}\end{array}$, while in the other the medial hydrogen is replaced:  $\begin{array}{c}\text{H}\quad\text{Cl}\quad\text{H}\\ \text{HC—C—CH}\\ \text{H}\quad\text{H}\quad\text{H}\end{array}$. These two chloropropanes yield in their turn two **methylpropanes** or **butanes**. Two such substances are said to be isomeric, or to exhibit isomerism with each other. The following list gives the names and formulæ of some of this series of hydrocarbons;

where the difference between their formulæ is CH_2, they are said to form a "homologous series."



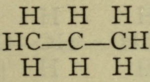
$$\begin{array}{c}\mathrm{H}\\ \mathrm{HCH}\\ \mathrm{H}\end{array}$$

Methane.



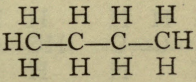
$$\begin{array}{ccc}\mathrm{H} & & \mathrm{H}\\ \mathrm{HC} & - & \mathrm{CH}\\ \mathrm{H} & & \mathrm{H}\end{array}$$

Ethane.



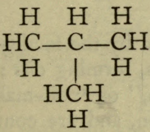
$$\begin{array}{ccccc}\mathrm{H} & & \mathrm{H} & & \mathrm{H}\\ \mathrm{HC} & - & \mathrm{C} & - & \mathrm{CH}\\ \mathrm{H} & & \mathrm{H} & & \mathrm{H}\end{array}$$

Propane.



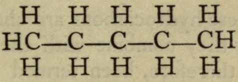
$$\begin{array}{ccccccc}\mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H}\\ \mathrm{HC} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{CH}\\ \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H}\end{array}$$

Butane.



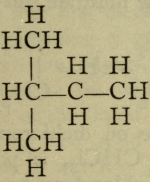
$$\begin{array}{ccccc}\mathrm{H} & & \mathrm{H} & & \mathrm{H}\\ \mathrm{HC} & - & \mathrm{C} & - & \mathrm{CH}\\ \mathrm{H} & & | & & \mathrm{H}\\ & & \mathrm{HCH} & & \\ & & \mathrm{H} & & \end{array}$$

Isobutane.



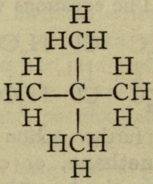
$$\begin{array}{ccccccccc}\mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H}\\ \mathrm{HC} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{CH}\\ \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H}\end{array}$$

Pentane.



$$\begin{array}{ccccc}\mathrm{H} & & & & \\ \mathrm{HCH} & & & & \\ | & & \mathrm{H} & & \mathrm{H}\\ \mathrm{HC} & - & \mathrm{C} & - & \mathrm{CH}\\ | & & \mathrm{H} & & \mathrm{H}\\ \mathrm{HCH} & & & & \\ \mathrm{H} & & & & \end{array}$$

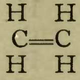
Isopentane.



$$\begin{array}{ccccc} & & \mathrm{H} & & \\ & & \mathrm{HCH} & & \\ \mathrm{H} & & | & & \mathrm{H}\\ \mathrm{HC} & - & \mathrm{C} & - & \mathrm{CH}\\ \mathrm{H} & & | & & \mathrm{H}\\ & & \mathrm{HCH} & & \\ & & \mathrm{H} & & \end{array}$$

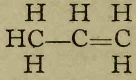
Tetramethyl-methane.

Chloromethane, if mixed with its own volume of chlorine and exposed to light, yields a **dichloromethane,** thus : $CH_3Cl + Cl_2 = CH_2Cl_2 + HCl$. This compound, which, like chloromethane, is also a gas soluble in ether, on treating its solution with sodium, loses chlorine and is converted into **ethylene,** thus : $CH_2Cl_2 + 4Na + Cl_2CH_2 = 4NaCl + \begin{array}{ccc}\mathrm{H} & & \mathrm{H}\\ \mathrm{C} & = & \mathrm{C}\\ \mathrm{H} & & \mathrm{H}\end{array}$. The carbon atom, it will be observed, is still a tetrad, but the two atoms are connected by a "double bond.” Homologues of ethylene are known, of which the following are a few :—



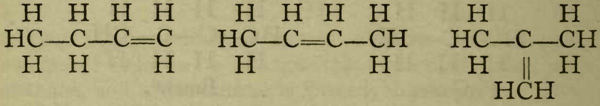
$$\begin{array}{cc}H & H\\ C & {=}C\\ H & H\end{array}$$

Ethylene.



$$\begin{array}{ccc}H & H & H\\ HC & -C & =C\\ H & & H\end{array}$$

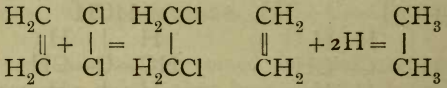
Propylene.



$$\begin{array}{cccc}H & H & H & H\\ HC & -C & -C & =C\\ H & H & & H\end{array}\qquad\begin{array}{cccc}H & H & H & H\\ HC & -C & =C & -CH\\ H & & & H\end{array}\qquad\begin{array}{ccc}H & & H\\ HC & -C & -CH\\ H & \Vert & H\\ & HCH & \end{array}$$

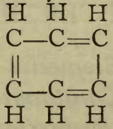
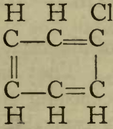
Butylenes.

These hydrocarbons are characterised by the facility with which they combine with the halogens, forming oils ; they have, therefore, been termed “olefines,” or “oil-makers.” They also unite with nascent hydrogen, and are converted into paraffins, as the members of the former group are termed. The equations which follow illustrate this :—



$$\begin{array}{c}H_2C\\ \Vert\\ H_2C\end{array} + \begin{array}{c}Cl\\ |\\ Cl\end{array} = \begin{array}{c}H_2CCl\\ |\\ H_2CCl\end{array}\qquad \begin{array}{c}CH_2\\ \Vert\\ CH_2\end{array} + 2H = \begin{array}{c}CH_3\\ |\\ CH_3\end{array}$$

By the further action of chlorine on dichloromethane, **trichloromethane**, or chloroform, $CHCl_3$, is produced. Chlorine can also be withdrawn from chloroform by sodium, and **acetylene**, C_2H_2, is formed : $HCCl_3 + 6Na + Cl_3CH = 6NaCl + HC{\equiv}CH$. Here the two carbon atoms are represented as united by a treble bond, and each carbon atom is still believed to remain tetrad. Acetylene is also characterised by the ease with which it unites with chlorine, forming a tetrachlorethane : $HC{\equiv}CH + 2Cl_2 = Cl_2HC{-}CHCl_2$. Here, also, other members of the series are known.

The passage of acetylene through a red-hot tube is attended by “polymerisation ;” that is, two or more molecules unite to form a more complex one. In this case, three molecules of acetylene combine to form a molecule of the formula C_6H_6, a compound to which the name **benzene** is applied. It is produced in large quantity by the distillation of coal, and is separated from coal-tar oil by distillation. Its carbon atoms are imagined to form a ring, because, among other reasons, it yields only one mono-chloro-substitution product:  gives on treatment with chlorine, Cl_2,  ; and as all the hydrogen atoms in the molecule are symmetrically arranged with respect to the carbon atoms, this condition is fulfilled.

The four first members of the methane series are gases ; those containing a greater number of atoms of carbon up to eleven are liquids, and the higher members are solids. The paraffin oil which is burned in lamps consists of a mixture of the liquid members, and paraffin candles largely consist of the solid members. They are all practically insoluble in water. The olefines have similar physical properties, and benzene is a volatile liquid. Iodine, sulphur, and phosphorus dissolve in the liquid hydrocarbons.

These and other hydrocarbons may be considered as somewhat analogous to the metals ; the analogy appears in the methods of formation and formulæ of their derivatives.

CHAPTER III

The Halides of the Elements—Double Halides —Endothermic Combinations—Hydrolysis —Oxidation and Reduction—Mass-Action.

The Halides.—Compounds of fluorine, chlorine, bromine, and iodine are thus named. They fall into classes when the elements are arranged according to the periodic system. Taking the chlorides as typical of the halides, we have the following table:—

										HCl
LiCl	$BeCl_2$	BCl_3	CCl_4	...	NCl_3	...	...	OCl_2	...	FCl?
NaCl	$MgCl_2$	$AlCl_3$	$SiCl_4$	PCl_5	PCl_3	SF_6	SCl_4	SCl_2	...	ClCl

KCl	$CaCl_2$	$ScCl_3$	$TiCl_4$	...	$AsCl_3$	...	$SeCl_4$	...	...	...
RbCl	$SrCl_2$	YCl_3	$ZrCl_4$	$SbCl_5$	$SbCl_3$	...	$TeCl_4$	$TeCl_2$	ICl_3	ICl
CsCl	$BaCl_2$	$LaCl_3$	$CeCl_4$	...	$ErCl_3$	...	...	...	...	...
...	...	$YbCl_3$	...	...	$BiCl_3$	...	...	...	...	...
...	...	...	$ThCl_4$	...	...	...	...	...	...	...

CuCl	$ZnCl_2$	$GaCl_3$	$GeCl_4$	VCl_5	VCl_3	...	...	$CrCl_2$	$MnCl_3$	...
AgCl	$CdCl_2$	$InCl_3$	$SnCl_4$	$NbCl_5$	$NbCl_3$	...	$MoCl_4$	$MoCl_2$	...	...
...	$GdCl_2$	...	$TbCl_4$	...	$PrCl_3$	...	...	$NdCl_2$	...	...
...	$HgCl_2$	$TlCl_3$	$PbCl_4$	$TaCl_5$	...	WCl_6	WCl_4	WCl_2	...	...
...	...	...	...	...	...	...	UCl_4	...	...	...

...	$FeCl_3$	$FeCl_2$	...	$CoCl_3$	$CoCl_2$	...	...	$NiCl_2$
...	$RuCl_3$	$RuCl_2$	...	$RuCl_3$	...	$PdCl_4$	...	$PdCl_2$
...	...	...	...	...	...	...	...	...
$OsCl_4$	$OsCl_3$	$OsCl_2$	$IrCl_4$	$IrCl_3$	...	$PtCl_4$	...	$PtCl_2$

Besides these compounds, which present considerable regularity, others exist which have less claim to order. Thus, KI_3 is also known; it is unstable, but CsI_3 is relatively stable. Again, $CuCl_2$ and $AuCl_3$ exist, also HgCl. In the next group, $GaCl_2$, InCl, and $InCl_2$ are also known, as well as TlCl. The following group contains $SnCl_2$ and $PbCl_2$; $PbCl_4$ is very unstable. Besides VCl_5 and VCl_3, VCl_4 and VCl_2 are also known; and in the next group, $CrCl_3$, $MoCl_3$, and $MoCl_5$, also WCl_5, UCl_3, and UCl_5. These compounds are difficult to classify.

The bromides and iodides, as well as the fluorides, corresponding to many of these chlorides in formula, are also known. Where they are of special interest, they will be alluded to in the sequel.

The **characteristic** of the **halides** of the **elements** of the **lithium group** is that they are all soluble white salts, crystallising in cubes. In dilute solution they are all ionised, and even in strong solution a large percentage of ions are present. Hence they all react as metal ions and as halogen ions. Thus, for instance, with silver nitrate, which is the usual test for ionic chlorine, the following reaction takes place: — $\overset{+}{Na}\overset{-}{Cl}.Aq + \overset{+}{Ag}\overset{-}{NO_3}.Aq = \overset{+}{Na}\overset{-}{NO_3}.Aq + AgCl$. Practically insoluble, and therefore practically non-ionised, silver chloride is precipitated, and free ions of sodium and the nitrate group remain in solution. If concentrated solutions are mixed, that portion which is ionised reacts; and as it is removed from solution, the originally non-ionised molecules of sodium chloride are ionised, because the solution becomes more dilute as regards sodium chloride, and they, too, enter into reaction. In a similar way, the alkali metal ions react in presence of a suitable reagent. Another point to be noticed is that these salts are not hydrolysed, that is, do not react with water to give hydroxide and acid to any appreciable extent, and the usual method of preparing them depends on these facts. They may all be obtained by the addition of halogen acids to the hydroxides or carbonates of the metals dissolved in water, thus: $\overset{+}{K}\overset{-}{OH}.Aq + \overset{+}{H}\overset{-}{Br}.Aq = \overset{+}{K}\overset{-}{Br}.Aq + H_2O$. It will be noticed that the water is not ionised, nor does it hydrolyse the potassium bromide; hence, on evaporation, as concentration increases, the number of ions of potassium and bromine becomes fewer and fewer, and after the water has been removed the pure dry salt is left. With a carbonate the action is similar. The equation is: $\overset{+}{Li_2}\overset{--}{CO_3}.Aq + 2\overset{+}{H}\overset{-}{I}.Aq = 2\overset{+}{Li}\overset{-}{I}.Aq + H_2O + CO_2$. In dilute solution the acid H_2CO_3 would be liberated; it is a very weak acid, *i.e.* it is comparatively very slightly ionised into $2\overset{+}{H}.Aq$ and $\overset{--}{CO_3}.Aq$; and, moreover, it readily decomposes into H_2O and CO_2; hence it is removed from the sphere of action as it is formed, and on evaporation the salt is left behind, as in the previous example.

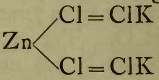
Sodium and potassium chlorides occur in nature; the former in the sea, which contains from 3.8 to 3.9 per cent. Deposits, which have undoubtedly been formed by the drying up of inland seas, are found in many places. At Stassfurth in S. Germany there are large deposits of all the salts present in sea-water, including common salt, chlorides and sulphates of magnesium, potassium, and sodium, and calcium sulphate; these have been deposited in layers in the order of their solubilities, the less soluble salts being deposited first. Bromides and iodides are also present in minute quantity in the residues from the evaporation of sea-water.

Solutions of the halides of the **beryllium group** of elements can also be made by acting on the hydroxides or carbonates of the metals with the halogen acid. To take barium chloride as an example, $\overset{++}{Ba}\overset{--}{CO_3}.Aq + 2\overset{+}{H}\overset{-}{Cl}.Aq = \overset{++}{Ba}\overset{-}{Cl_2}.Aq + H_2O + CO_2$. Now barium carbonate is nearly insoluble in water, but the portion which dissolves is ionised; and, as explained above, when the portion which is ionised has reacted, its place is taken by more of the carbonate entering into solution ; so that finally all is changed into chloride. With the hydroxides, the same kind of reaction takes place:

$$\overset{++}{Ca}(\overset{-}{OH})_2.Aq + 2\overset{+}{H}\overset{-}{Br}.Aq = \overset{++}{Ca}\overset{-}{Br}_2.Aq + 2H_2O.$$

These salts are also white and soluble in water. There is, however, one exception, namely, calcium fluoride, CaF_2, which occurs native as fluor- or Derbyshire spar. It forms colourless cubical crystals, and is the chief compound of fluorine. It is produced by precipitation: $\overset{++}{Ca}\overset{-}{Cl}_2.Aq + 2\overset{+}{K}\overset{-}{F}.Aq = CaF_2 + 2\overset{+}{K}\overset{-}{Cl}.Aq$. The calcium fluoride is non-ionised, and comes down in an insoluble form.

Water of Crystallisation.—The other halides of this group crystallise with water of crystallisation ; its amount varies from 7 molecules, as in $BaI_2.7H_2O$, to 1 as in $ZnCl_2.H_2O$. The retention of this so-called "water of crystallisation" has not yet been satisfactorily explained. It was for long believed that such compounds were "molecular," as opposed to atomic ; that is, that the water molecules combined as wholes with the salt, and not by virtue of their atoms ; but it is more probably to be explained by the tetravalency of oxygen, although even with this assumption it is not easy to ascribe satisfactory constitutional formulæ in all cases. It must at the same time be assumed that the halogen atoms are of a higher valency than unity ; possibly triad, or even pentad.

These salts are hydrolysed in solution to a small extent ; thus a solution of magnesium chloride, besides containing a large number of ions, has also reacted with the water to form hydroxide and hydrogen chloride: $MgCl_2 + 2H(OH) = Mg(OH)_2 + 2HCl$. As the solution becomes concentrated on evaporation, the hydrogen chloride volatilises with a part of the water ; and a mixture, or rather a compound, of the oxide and chloride remains. Hence these chlorides cannot be obtained in a pure state by evaporating their solutions. They exhibit another property, however, which makes it possible to obtain them in a pure state, namely, the power of forming "**double halides.**" This property is not well marked with the halides of calcium, barium, and strontium, but the halides of beryllium, magnesium, zinc, and cadmium are notable in this respect. We have, for example, $MgCl_2.KCl.6H_2O$, $ZnCl_2.NH_4Cl$, and many similar bodies. In solution, such compounds are mainly ionised into their simple ions, but on evaporation the non-ionised salt separates in crystals, and is not subject to hydrolysis. Hence such salts can be dried without decomposition. The ammonium salts, when sufficiently heated, lose ammonia and hydrogen chloride by volatilisation, and the anhydrous halide is left: $MgCl_2.NH_4Cl = MgCl_2 + NH_3 + HCl$. The mode of combination of these double salts is possibly owing to the fact that the halogens are capable of acting as triads ; thus 

$$\mathrm{Zn}\begin{array}{l}\diagup \mathrm{Cl}=\mathrm{ClK}\\ \diagdown \mathrm{Cl}=\mathrm{ClK}\end{array}$$

may be taken as the constitutional formula of that particular salt.

The **mono-halides** of **copper, silver,** and **gold** may be attached to the first group ; and if that is done, the mono-halides of **mercury** must also be included. These compounds are all insoluble in water, and are consequently obtained by precipitation or by heating the higher halides, where these exist. Thus CuCl and AuCl are obtained by cautiously heating $CuCl_2$ and $AuCl_3$; they are white insoluble powders. **Cuprous chloride** is more easily obtained by removing half the chlorine from cupric chloride dissolved in concentrated hydrochloric acid, by digesting it with metallic copper: $CuCl_2.2HCl.Aq + 2HCl.Aq + Cu = Cu_2Cl_2.4HCl.Aq$, a brown compound, which is decomposed by water into Cu_2Cl_2 and $4HCl.Aq$; the cuprous chloride is thrown down as a snow-white powder. With silver and mercury, the chlorides AgCl and HgCl are formed by precipitation from the respective nitrates, $AgNO_3$ and $HgNO_3$, on addition of soluble chlorides. The bromides and iodides are similarly formed, and are also insoluble.

There are several interesting points connected with these halides. First, as regards their colour; the chlorides are white; cuprous bromide is greenish brown, while the bromides of silver, gold, and mercury are yellow; and cuprous iodide is brownish, and the iodides of the other metals darker yellow than the bromides. It appears as if the colour was influenced both by the metal and by the halogen. Next, the chlorides of copper and mercury give evidence of possessing the double formulæ Cu_2Cl_2 and Hg_2Cl_2, which would imply that the metals were only pseudo-monads, and that the structural formulæ should be $Cl{-}Cu{-}Cu{-}Cl$ and $Cl{-}Hg{-}Hg{-}Cl$; and this would correspond with the fact that the chlorides $CuCl_2$ and $HgCl_2$ are also known; but, on the other hand, as AgCl in the state of gas has the simple formula given to it, it may be that it is the halogen which forms the bond of union between the two half-molecules, thus: $CuCl{=}ClCu$. Silver forms no higher halides.

The fluorides of these elements differ from the others in being soluble in water; they are prepared from the oxides with hydrofluoric acid. They are very difficult to dry, for they undergo the reverse reaction, and are hydrolysed into oxide and hydrogen fluoride on evaporation.

Copper and **mercury** also function as **dyads**; that is, their ions are capable of carrying a double electric charge under certain circumstances. What the mechanism of this change is, we do not know; but the change in valency can be induced by presenting to the element a larger amount of halogen, if it is desired to increase the valency, or by removing halogen if the opposite change is required. The addition of halogen to the mono-halide is in each case an exothermic change, and its converse is an endothermic one. Cuprous or mercurous chloride, heated in a current of chlorine changes to cupric or mercuric chloride, and the converse change can be brought about by heating the higher halide in a current of hydrogen, or by exposing the lower halide to the action of nascent hydrogen; but it is difficult to prevent the action in the latter case from going too far and yielding the metal. A solution of cupric chloride saturated with sulphurous acid in presence of hydrochloric acid, and then diluted with water, gives a precipitate of cuprous chloride: $2CuCl_2.Aq + H_2SO_3.Aq + 2HCl.Aq + H_2O = Cu_2Cl_2.4HCl.Aq + H_2SO_4.Aq$. The sulphurous acid removes oxygen from water, liberating hydrogen in presence of the cupric chloride, and the latter is deprived of half its chlorine and reduced to cuprous chloride. Similarly, stannous chloride forms a reducing agent for mercuric chloride: $2HgCl_2.Aq + SnCl_2.Aq = Hg_2Cl_2 + SnCl_4.Aq$. The converse change can be produced by exposing the lower halide in presence of halogen acid to the action of nascent oxygen: $Cu_2Cl_2 + 2HCl.Aq + O = 2CuCl_2.Aq + H_2O$. This oxygen in the case of copper may be molecular, O_2, but for the formation of the higher halide of mercury, it must be derived from some substance capable of parting readily with oxygen, such as nitric acid.

Cupric iodide is very unstable, and readily yields up iodine, forming cuprous iodide. On mixing cupric chloride with potassium iodide, the cuprous iodide is precipitated: $2\overset{++}{Cu}\overset{-}{Cl_2}.Aq + 4\overset{+}{K}\overset{-}{I}.Aq = \overset{+}{Cu_2}\overset{-}{I_2} + 4\overset{+}{K}\overset{-}{Cl}.Aq + I_2$. It is to be noticed that the dyad cupric ions have lost two charges, and that these have neutralised the two negative charges of the iodine ions, causing them to be precipitated. (Inasmuch as the cuprous iodide is insoluble, it should not have had the ionic signs attached; but they have been kept in order to show the changed valency.) **Mercuric iodide** is an insoluble scarlet precipitate, and is therefore best produced by precipitation. It dissolves, however, in a solution of potassium iodide, forming a double salt, of which more shortly.

Auric chloride contains triad gold, and thus has the formula $AuCl_3$. It is not produced by the direct action of chlorine on gold, because the temperature of attack is above the temperature at which the compound is decomposed. But it is possible to volatilise gold in a current of chlorine, because a few molecules escape decomposition and are volatilised along the tube through which the chlorine is passed, and on cooling the gold is deposited, owing to the decomposition of the chloride at a lower temperature. It may appear paradoxical that the chloride is stable at a higher temperature than that at which it decomposes; but it is to be presumed that the difference of temperature between one favourable to an exothermic and to an endothermic action is very small; and as endothermic substances increase in stability on rise of temperature, the chloride is capable of volatilisation; on cooling it becomes unstable and undergoes decomposition with deposition of gold. The usual method of preparing this salt is to dissolve gold in a mixture of nitric and hydrochloric acids. This mixture yields ionic chlorine, the negative charge of which neutralises the positive charges of the gold; but there are corresponding negative charges set free, which are transferred to the ion $\overset{-}{N}O_3$ of the nitric acid, converting it into $2\overset{--}{O}$, with its four negative charges. The latter combines with the hydrogen, forming electrically neutral water: $3\overset{+}{H}\overset{-}{Cl} + \overset{+}{H}\overset{-}{NO_3}.Aq + Au = 2H_2O + \overset{+++}{Au}\,\overset{-}{Cl_3}.Aq + NO$.

Auric chloride forms dark red crystals; it is soluble in water, and when mixed with chlorides of the alkali metals forms a set of salts termed **aurichlorides.** The potassium salt, for example, has the formula $KAuCl_4$; it is soluble in water, but, unlike the "double salts," such as $MgCl_2.2KCl$, already alluded to, it is ionised by water, not into simple ions like these, but into the ions $\overset{+}{K}$ and the complex group $\overset{-}{AuCl_4}$. At the same time there exists in the solution a small number of simple ions, so that on electrolysis gold is deposited at the kathode, but the primary effect of the current is to send the aurichloric ions to the anode. The solution of **mercuric iodide in potassium iodide,** of which mention was made before, is a half-way example of the same kind. Its solution contains ions of $\overset{+}{K}$ and $\overset{-}{HgI_3}$, but these are mixed with a much larger proportion of the simple ions, $\overset{+}{K}$ and $\overset{-}{I}$ and $\overset{++}{Hg}$ and $\overset{-}{I_2}$. All grades of such salts are known ; indeed it is probable that the double salts, such as magnesium-potassium chloride, contain a small number of complex ions of $\overset{-}{MgCl_3}$.

These halides have been considered at length because they form types of the others. Use will be made of the examples given in treating of the remaining halides.

We have seen that the halides may undergo either ionisation or hydrolysis, or both at once. The ionisation may be more or less complete, and the hydrolysis is promoted by dilution and by a high temperature. The remaining halides display both these kinds of behaviour, and according as one or the other prevails, the methods of preparing them are affected. In certain cases, moreover, the halides form compounds with other halides, usually those of the alkali metals or hydrogen, which are less apt to be hydrolysed, and yield different complex ions. The **halides of carbon** and **nitrogen** belong to neither of these classes, for they are insoluble in and unacted on by water. As neither carbon nor nitrogen is acted on by the halogens (excepting that carbon burns in fluorine), they must be prepared indirectly by acting on one of their compounds with the halogen. Methane or carbon disulphide is chosen for the former, and ammonia in preparing the latter. By passing a current of chlorine saturated with the vapour of carbon disulphide through a red-hot tube, the chlorides of both carbon and sulphur are formed : $CS_2 + 3Cl_2 = CCl_4 + S_2Cl_2$. On treatment with water the sulphur chloride is decomposed, while the **chloride of carbon** may be distilled off ; it forms a colourless liquid boiling at 76.7°. Its smell resembles that of the closely allied chloroform, $CHCl_3$, and it is also possessed of anæsthetic properties. For the preparation of **nitrogen chloride** a jar of chlorine is inverted over a saturated solution of ammonia in water; oily drops are formed which settle to the bottom of the vessel: $NH_3.Aq + 3Cl_2 = NCl_3 + 3HCl.Aq$; the HCl unites with ammonia, forming ammonium chloride.

Endothermic Combination.—This body is fearfully explosive, for its formation is attended by great absorption of heat; but during its formation the reagents do not grow cold; for the formation of ammonium chloride is a highly exothermic reaction, and the amount of heat evolved by its formation is greater than that of the equivalent amount of chloride of nitrogen; hence the change as a whole is accompanied by evolution of heat. It is thus that endothermic compounds are usually formed: by virtue of a simultaneous action in which heat is evolved. The slightest shock causes the decomposition of such endothermic bodies; if one single molecule is decomposed, it evolves heat and brings about the decomposition of its neighbours; and as all the molecules are in close proximity to each other, and as the products, nitrogen and chlorine, are both gases, and are, moreover, much raised in temperature by being set free, the decomposition is accompanied by sudden and enormous expansion. **Nitrogen iodide,** prepared by adding a solution of iodine to aqueous ammonia, is a black solid of the formula $NI_3.NH_3$; it is also explosive.

The **fluorides** of **boron** and **silicon** are both produced by the action of a strong solution of hydrofluoric acid on the oxides; but it is necessary to have some agent present to withdraw water, such as concentrated sulphuric acid. These compounds are both gaseous. Their formation is shown by the equations: $B_2O_3 + 6HF = 2BF_3 + 3H_2O$; $SiO_2 + 4HF = SiF_4 + 2H_3O$. If the water is not withdrawn, combination ensues between the fluoride and hydrogen fluoride, with formation of HBF_4 or H_2SiF_6, named respectively **hydroborofluoric,** and **hydrosilicifluoric** acids thus: $4BF_3 + 3H_2O = 3HBF_4 + H_3BO_3$; $3SiF_4 + 3H_2O = 2H_2SiF_6 + H_2SiO_3$. These compounds ionise into $\overset{+}{H}$-

ions, and the complex ions $\overset{-}{\mathrm{BF}_4}$ and $\overset{--}{\mathrm{SiF}_6}$; and many salts are known in which metals replace the hydrogen. They are similar in kind to potassium aurichloride.

The other **halides** of **boron** and **silicon**, and also of **phosphorus**, **sulphur**, **selenium**, **tellurium**, and **iodine**, react at once with water, forming hydrogen halide and an acid. The equations are as follows:—

$$\begin{aligned}
\mathrm{BCl_3 + 3H_2O.Aq} &= \mathrm{B(OH)_3.Aq + 3HCl.Aq};\\
\mathrm{SiCl_4 + 3H_2O.Aq} &= \mathrm{O{=}Si(OH)_2 + 4HCl.Aq};\\
\mathrm{PCl_3 + 3H_2O.Aq} &= \mathrm{P(OH)_3.Aq + 3HCl.Aq};\\
\mathrm{PCl_5 + 4H_2O.Aq} &= \mathrm{O{=}P(OH)_3.Aq + 5HCl.Aq};\\
\mathrm{2S_2Cl_2 + 2H_2O.Aq} &= \mathrm{O{=}S(OH)_2.Aq + 4HCl.Aq};\\
&\qquad \mathrm{+\,3S};\\
\mathrm{2TeCl_2 + 3H_2O.Aq} &= \mathrm{O{=}Te(OH)_2.Aq + 4HCl.Aq}\\
&\qquad \mathrm{+\,Te};\\
\mathrm{SCl_4 + 3H_2O.Aq} &= \mathrm{O{=}S(OH)_2.Aq + 4HCl.Aq};\\
\mathrm{5ICl_3 + 9H_2O.Aq} &= \mathrm{3HIO_3.Aq + 15HCl.Aq + I_2}.
\end{aligned}$$

It is to be noticed that where a hydroxy-compound corresponding to the halide is capable of existence, it is formed; if not, excess of the element is set free. Hence none of these halides can be prepared by acting on the hydroxide with a halogen acid; they are all made either by the direct action of the halogen on the element, or by what comes to the same thing, the action of the halogen on a strongly heated mixture of the oxide of the element with carbon. Boron, silicon, and phosphorous chlorides are volatile liquids; they fume in the air owing to their action on the water-vapour. $\mathrm{S_2Cl_2}$ is a yellow liquid; when saturated with chlorine at a low temperature, $\mathrm{SCl_2}$ and $\mathrm{SCl_4}$ are successively formed; but on rise of temperature they dissociate into the lower chloride. ICl is a black solid, converted by excess of chlorine at a low temperature into $\mathrm{ICl_3}$, a yellow solid, which easily dissociates into ICl and $\mathrm{Cl_2}$; and $\mathrm{PCl_5}$ is a pale yellow solid, volatile at a high temperature in a perfectly dry atmosphere without dissociation, but resolved by the least trace of moisture into PCl_3 and Cl_2.

Valency of Elements.—We may remark here the gradual increase of valency as we pass from left to right in the periodic table. Lithium is a monad, with its congeners; the elements of the beryllium group are dyads; boron a triad; carbon a tetrad; phosphorus acts as pentad as well as triad; sulphur, as a pseudo-monad, a dyad, and a tetrad; and **Moissan** has lately shown that sulphur burns in fluorine, forming a very stable hexafluoride, SF_6; while iodine forms a monochloride and a trichloride, and probably also a pentafluoride and a heptafluoride.

Passing back to the boron group, if it is desired to form anhydrous chloride, it is necessary either to heat the element, or its oxide mixed with charcoal, in a current of chlorine, or, except in the case of boron, to prepare a double salt of the chloride with ammonium chloride, and to volatilise the latter after driving off the water; the aqueous chlorides are formed by dissolving the oxides or hydroxides in hydrochloric acid. Thallium forms monohalides, sparingly soluble in cold water, and thereby attaches itself to the copper group.

Almost the same remarks apply to the elements of the carbon group; solutions of the chlorides, with exception of those of carbon and silicon, are obtained from the element and hydrochloric acid or from the hydroxide, and they cannot be dried without reacting wholly or partially with water. For instance, **titanium chloride**, on careful addition of water, can become $ClTi(OH)_3$, $Cl_2Ti(OH)_2$, $Cl_3Ti(OH)$, all of which are intermediate products between the tetrachloride and the tetrahydroxide; such compounds are termed "basic chlorides." Anhydrous **stannic chloride** is a fuming liquid, formed by the distillation of a mixture of the metal with mercuric chloride or by heating the metal in a stream of chlorine. **Lead tetrachloride** is a very unstable liquid, formed from the tetracetate, $Pb(C_2H_3O_2)_4$, by converting it into the double ammonium salt with a mixture of ammonium chloride and concentrated hydrochloric acid; this salt, $(NH_4)_2PbCl_6$, is then decomposed by concentrated sulphuric acid, when the tetrachloride separates as a heavy liquid. It at once decomposes into $PbCl_2 + Cl_2$ on warming; hence PbO_2, when warmed with hydrochloric acid, undergoes the change: $PbO_2 + 4HCl.Aq = PbCl_2 + Aq + Cl_2$.

Tin and **lead** resemble elements of the zinc group in forming **dichlorides**. On dissolving tin in hydrochloric acid the dichloride is formed; and a solution of the tetrachloride, when exposed to the action of nascent hydrogen, yields the lower chloride. This action may be thus formulated:— $\overset{++++}{Sn}\,\overset{-}{Cl_4}.Aq + 2\overset{+}{H} = \overset{++}{Sn}\overset{-}{Cl_2}.Aq + \overset{+}{H}\overset{-}{Cl}.Aq$. **Stannous chloride** is a white, soluble salt, crystallising with water of crystallisation. **Lead dichloride**, on the other hand, is sparingly soluble in cold water; it is formed when a soluble lead salt, such as the nitrate, is mixed with the solution of a chloride: $Pb(NO_3)_2.Aq + 2NaCl.Aq = PbCl_2 + 2NaCl.Aq$. The bromide and the iodide are also sparingly soluble, and are similarly produced.

With arsenic and the remaining members of that group we may notice the same characters: the anhydrous chlorides produced by the action of chlorine on the element, or, when it is not available, on a mixture of the oxide with carbon at a red heat; the aqueous solution produced by dissolving the oxide or hydroxide in hydrochloric acid. Basic chlorides are also known, *e.g.* $ClAsO$, $ClSbO$, and $ClBiO$, from the trichlorides; and $OPCl_3$, and $OSbCl_3$, from the pentachlorides, on reacting with a small amount of water.

Mass-Action.—The action of mass, that is, the quantity of a compound in unit volume, is well illustrated by the action of water on antimonious chloride. A solution of this salt in hydrochloric acid gives a precipitate on adding water: $SbCl_3.nHCl.Aq + H_2O = OSbCl + (n + 2)HCl.Aq$. Here the increase in the number of molecules of water causes the precipitation of the basic chloride; on adding more hydrochloric acid, however, so as to increase its active mass, the reaction is reversed, and the precipitate redissolves: $OSbCl + (n + 2)HCl.Aq = SbCl_3.Aq.nHCl + H_2O$. Above a certain concentration of water SbOCl is stable; above a certain concentration of hydrogen chloride, $SbCl_3$.

The higher **halides** of **molybdenum, tungsten,** and **uranium,** themselves prepared by the action of halogen on the element, yield the lower halides on heating. They are volatile, coloured bodies, soluble in water; the higher ones are decomposed by water.

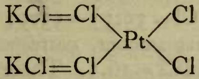
The elements **chromium, manganese, iron, cobalt,** and **nickel,** although not all belonging to the same series, show, nevertheless, a gradation of properties. The **dihalides** of all are known in the dry state; they are most readily obtained by heating the metal in a current of hydrogen halide, if required anhydrous; or if in solution or crystallised with water, by dissolving the oxide or carbonate in the halogen acid and evaporating until crystallisation ensues. As examples: $Fe + 2HCl = FeCl_2 + H_2O$; $MnCO_3 + 2HBr.Aq = MnBr_2.Aq + H_2O + CO_2$.

The **trihalides** are best made by heating the elements in a current of halogen, if required anhydrous; if in solution, by dissolving the oxide or hydroxide in the halogen acid. The trihalides of manganese and cobalt are very unstable; and if the corresponding oxides be treated with halogen acid, a portion of the halogen is evolved, thus: $Fe_2O_3 + 6HCl.Aq = 2FeCl_3.Aq + 3H_2O$; $Mn_2O_3 + 6HCl.Aq = 2MnCl_3Aq + 3H_2O$. But $MnCl_3.Aq$ gradually decomposes, especially if temperature is raised, thus: $2MnCl_3.Aq = 2MnCl_2.Aq + Cl_2$. And if MnO_2 be employed, chlorine is evolved from the outset: $2MnO_2 + 8HCl.Aq = 2MnCl_3.Aq + 4H_2O + Cl_2$; the $MnCl_3$ decomposing further on standing or on rise of temperature. With Co_2O_3 a transient brown coloration is noticeable on adding hydrochloric acid, implying the momentary formation of $CoCl_3.Aq$; but it is at once resolved into $CoCl_2.Aq$ and free chlorine.

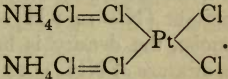
Oxidation and Reduction.—As already remarked, the raising of the valency of an element is often spoken of as "oxidation;" the reducing of the valency, as "reduction." The tendency of chromous halides to transform into chromic compounds is so great, that it is not possible to expose them to air without the change taking place, and consequently the reduction of chromic compounds to chromous is a difficult operation. But with iron, both classes of compounds have nearly equal stability; hence oxidation and reduction play a great part in their formation. The action of nascent hydrogen from any source reduces ferric halide into ferrous: $FeCl_3.Aq + H = FeCl_2.Aq + HCl.Aq$. Similarly, a ferrous halide, in presence of halogen acid and either free or nascent oxygen, is oxidised to a ferric: $2FeCl_2.Aq + 2HCl.Aq + O = 2FeCl_3.Aq + H_2O$. Or the halogen itself may be used to effect the change: $2FeCl_2.Aq + Cl_2 = 2FeCl_3.Aq$. On evaporating these solutions, hydrolysis takes place partially; thus ferric chloride yields compounds of a basic character, such as $(OH)FeCl_2$, $(OH)_2FeCl$, which are partly hydroxide, partly chloride. This statement applies to the halides of all these metals.

Colour of Ions.—The triad and dyad ions in the case of these metals exhibit remarkable differences of colour. Thus chromous ions are blue, chromic, green; basic ferric ions are orange-yellow, ferrous, pale green; manganic, brown, manganous, pale pink; cobaltous, red, and nickelous, grass-green. Hence a change in the ionic charge of the metallic ion is accompanied by a striking colour-change.

The **halides** of the **palladium** and **platinum groups** of **metals** closely resemble in character those of gold, which have already been described. The dihalides of the palladium group are all soluble, save PdI_2, which is prepared by precipitation with potassium iodide. Nitro-hydrochloric acid yields the higher chloride; it remains on evaporation. These form with chlorides of the alkalies double salts, *e.g.* $RuCl_3.2HCl$, $RhCl_3.2HCl$, and $PdCl_4.2HCl$; the latter are probably ionised as $\overset{+}{K}\overset{+}{K}$ and $\overset{-\,-}{Pd}Cl_6$, &c. Chlorine also acts directly on red-hot metals of the platinum group, forming a mixture of chlorides; these, on heating, lose chlorine, giving lower chlorides. Solutions of the halides can also be prepared by the action of the halogen acid on the respective oxides. On heating to a high temperature, all these halides are decomposed into the metal and halogen. The compounds K_2PtCl_6 and $(NH_4)_2PtCl_6$ require special mention; they are orange salts, nearly insoluble in water, and are used as tests for potassium and ammonium, and also as a precipitant in estimating these ions. Their existence is probably to be ascribed to the power possessed by chlorine of sometimes acting as a triad, and the structural formula is believed to be



and



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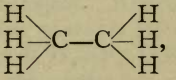
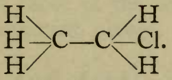
Halides of certain *complex groups* are also known. When these contain oxygen or hydroxyl, (OH), they are generally termed basic salts or halo-acids; they will be considered later. The others may be divided into two classes: those like ammonium halides, and those derived from hydrocarbons.

Ammonium and phosphonium halides.—These halides, which are formed by direct addition of the hydrogen halide to ammonia or to phosphine, closely resemble in colour, in crystalline form (cubic), and in reactions, the halides of the lithium group of metals. On mixing a solution of ammonia and hydrochloric acid, for example, the combination occurs: $NH_3.Aq + HCl.Aq = NH_4Cl.Aq$; and on evaporating the solution to dryness, ammonium chloride is left in an anhydrous state. From the conductivity of ammonia solution, it is known to contain a certain amount of NH_4OH in an ionised condition; and the equation may be written: $\overset{+}{NH_4}\overset{-}{OH}.Aq + \overset{+}{H}\overset{-}{Cl}.Aq = \overset{+}{NH_4}\overset{-}{Cl}.Aq + H_2O$.

As the hydroxyl ion is removed from the solution by the formation of practically non-ionised water, more and more ammonium hydroxide is formed to maintain equilibrium between the $NH_3.Aq$ and the $NH_4OH.Aq$; and the whole is ultimately transformed. The rate of transformation, however, is a very rapid one. Combination has been shown not to take place between perfectly dry ammonia and dry hydrogen chloride ; hence it does not seem unlikely that ionisation may occur, either in the gaseous state, or more probably on the surface of the vessel in the condensed layer of moisture which appears always to adhere to all solid surfaces. Once started, combination occurs continuously until the reaction is complete. Ordinarily "dry" ammonia, however, at once gives a dense cloud with hydrogen chloride, bromide, or iodide. Again, perfectly dry ammonium chloride has the vapour-density 26.25, corresponding to the molecular weight $(N = 14 + H_4 = 4 + Cl = 35.5) = 53.5$; whereas, if moist, the density is half that amount, corresponding with a mixture of $NH_3 = 17$ and $HCl = 36.5$. These compounds have densities of 8.5 and 18.25 respectively, and a mixture in equal proportions of each has a density the mean of the two, viz., 13.125. It appears necessary that ionisation into $\overset{+}{NH_4}$ and $\overset{-}{Cl}$ should take place before dissociation into NH_3 and HCl is possible. The electrically neutral body NH_4Cl can volatilise unchanged ; the ions $\overset{+}{NH_4}$ and $\overset{-}{Cl}$ are incapable of volatilisation as such, and in volatilising unite their opposite charges, and form the two electrically neutral compounds HCl and NH_3.

Phosphine, PH_3, also unites with hydrogen **chloride,** but only under high pressure, at the ordinary temperature. On the other hand, **phosphonium iodide,** PH_4I, is produced by the union of phosphine with hydrogen iodide under atmospheric pressure ; it forms white, cubical crystals, which, like ammonium chloride, dissociate when heated. The hydrides of arsenic and antimony form no such compounds.

It must be assumed that these compounds are formed with change of valency of the nitrogen or phosphorus; the triad becomes pentad; the $N^{III}H_3$ becomes $H_4N^{V}Cl$. On distilling with sodium hydroxide or slaked lime, water is formed, and the element is reduced to its original triad condition, thus: $\overset{+}{N}H_4\overset{-}{Cl}.Aq + \overset{+}{Na}\overset{-}{OH}.Aq = \overset{+}{N}H_4\overset{-}{OH}.Aq + \overset{+}{Na}\overset{-}{Cl}.Aq$, and $\overset{+}{N}H_4\overset{-}{OH}.Aq = NH_3 + H_2O.Aq$, two electrically neutral bodies.

Carbon shows no such tendency to change valency. The hydrocarbons of the methane series are "saturated," *i.e.* they have no tendency to take up any other element. Hence halogen must replace hydrogen. This can be done either directly, by the action of the halogen on the hydrocarbon, as, for instance, $CH_4 + Cl_2 = CH_3Cl + HCl$; or indirectly, by the action of the halogen acid on the hydroxide: $CH_3OH + HCl = CH_3Cl + H_2O$. Such hydroxides are termed **alcohols**; that derived from ethane, C_2H_6, is the ordinary anhydrous alcohol of commerce; its formula is C_2H_5OH, and the corresponding chloride of ethyl is C_2H_5Cl. It will be remembered that the structural formula of ethane is , and that of ethyl chloride is  There is, however, a difference between the formation of ethyl chloride, for example, and of sodium chloride. Whereas sodium chloride is ionised in solution in water, ethyl chloride is insoluble, and is therefore non-ionised. Hence the action is a slow one; the alcohol is saturated with hydrogen chloride, allowed to stand for some hours, and distilled; ethyl chloride, being volatile, passes over; it is a gas, condensing at about 12° to a mobile colourless liquid. It is probable that the hydrogen chloride is ionised in solution in alcohol; the alcohol is also possibly ionised to a minute extent;

water is formed by the union of the hydrogen and hydroxyl ions, and non-ionised ethyl chloride distils over: $\overset{+}{C_2H_5}\overset{-}{OH} + \overset{+}{H}\overset{-}{Cl}.Alc = H_2O + C_2H_5Cl$. But this suggestion, it must be admitted, is somewhat speculative, and is based only on analogy with reactions of a more familiar nature.

The formation of some of the halogen compounds of the olefines, and of hydrocarbons of the acetylene and benzene series, has already been alluded to on p. 48.

CHAPTER IV

Hydroxides and Acids—"Insoluble Substances"—Indicators—Preparation of Basic Oxides—Properties of the Basic Oxides and Hydroxides—Sulphides—The "Solubility-Product"—Basic Oxides and Hydroxides of Complex Groups: Alcohols, Aldehydes, Ethers; and Sulphines, Amines and Phosphines.

The Oxides and Hydroxides, Sulphides and Hydrosulphides, Selenides and Tellurides.—Owing to the dyad valency of oxygen, sulphur, selenium, and tellurium, compounds of these elements are more numerous than those of the halogens. And whereas double halides of hydrogen and other elements are not numerous, being confined to such bodies as H_2SiF_6, HBF_4, H_2PtCl_6, and a few others, those of the oxides are very numerous, and form two important classes, the "hydroxides" and the "acids."

Hydroxides and Acids.—Members of both these classes may be regarded as hydroyxl, that is, water minus one atom of hydrogen, –OH, in combination with elements, but they differ radically in that the true hydroxides ionise into element and hydroxl, thus: $\overset{+}{Na}\overset{-}{OH}.Aq$, $\overset{++}{Ca}(\overset{-}{OH})_2.Aq$, $\overset{+++}{Bi}(\overset{-}{OH})_3$; whereas acids ionise into hydrogen and a negatively charged radical, thus: $\overset{+}{H}\overset{-}{OCl}.Aq$, $\overset{+}{H}\overset{-}{NO_3}.Aq$, $\overset{+}{H}(\overset{-}{H}\overset{-}{S}O_4).Aq$, $\overset{+}{H}_2\overset{--}{SO}_4.Aq$, and many others. There are certain hydroxides in which the ionisation may take either form; such compounds are said to be either "basic" or "acid" according to circumstances; thus, aluminium hydroxide, $\overset{+++}{\text{Al}}(\overset{-}{\text{OH}})_3$, is basic; with hydrochloric acid it reacts in the following manner: $\overset{+++}{\text{Al}}(\overset{-}{\text{OH}})_3.\text{Aq} + 3\overset{+}{\text{H}}\overset{-}{\text{Cl}}.\text{Aq} = \overset{+++}{\text{Al}}\,\overset{-}{\text{Cl}}_3.\text{Aq} + 3\text{H}_2\text{O}$; on the other hand, when caustic soda is presented to aluminium hydroxide, it forms sodium aluminate, $\text{NaAlO}_2.\text{Aq}$, a derivative of the acid $\text{HAlO}_2.\text{Aq}$, which is formed from Al(OH)_3 by loss of water: $\text{Al(OH)}_3 = \text{O=AlOH} + \text{H}_2\text{O}$. The ions in the latter case are $\overset{+}{\text{H}}$ and $\overset{-}{\text{AlO}_2}$, and the reaction takes place between HAlO_2 and NaOH, thus: $\overset{+}{\text{H}}\overset{-}{\text{AlO}_2}.\text{Aq} + \overset{+}{\text{Na}}\overset{-}{\text{OH}}.\text{Aq} = \overset{+}{\text{Na}}\overset{-}{\text{AlO}_2}.\text{Aq} + \text{H}_2\text{O}$. It is generally the case that the acids are derived from hydroxides which have lost a portion of their hydrogen as water. They are, like O=AlOH, partly oxide, partly hydroxide.

"Insoluble Substances."—The hydroxides are, with some exceptions, generally spoken of as insoluble in water. The word "soluble" is a relative term; it is probable that very few, if any, substances are absolutely insoluble. Silver chloride is usually regarded as wholly insoluble in water, but pure water shaken up with that salt acquires increased conductivity, showing that some chloride must have gone into solution. In one of the equations given above, Al(OH)_3 is followed by "Aq," implying that it is dissolved and ionised in solution. This method of writing is perfectly correct for the portion which is dissolved, but that constitutes only a very minute fraction of the whole. What is dissolved, however, *is* ionised and enters into reaction, and when it has been removed, as in the equation given, with formation of practically non-ionised water-molecules, its place is taken by more: equilibrium tends to establish itself between the dissolved portion and the portion remaining undissolved. We know well that if excess of common salt be placed at the bottom of a vessel of water it will not all dissolve, but, as the dissolved portion diffuses away into the upper layers of water, its place is taken by fresh salt, which dissolves, until, if sufficient time be given, the whole solution becomes saturated with salt. Similarly, the removal of the aluminium—as ions, it may be—and of the hydroxyl of the aluminium hydroxide, $Al(OH)_3$, as water, on treatment with an acid, causes a fresh portion of the hydroxide to go into solution, and this continues to go on until all has undergone reaction.

The hydroxides of the elements may be classified like the halides; the analogy between the formulæ is seen on comparing the tables on pp. 72, 73, with those on p. 50.

Oxygen compounds of fluorine are wanting.

$[Cl(OH)_7]$,	$[Cl(OH)_5]$,	$[Cl(OH)_3]$,	$Cl(OH)$.
$[OCl(OH)_5]$,	$[OCl(OH)_3]$,	$OCl(OH)$,	Cl_2O.
$[O_2Cl(OH)_3]$,	$O_2Cl(OH)$,	$[Cl_2O_3]$.	
$O_3Cl(OH)$,	$[Cl_2O_5]$.		
$[Cl_2O_7]$.			

The formulæ enclosed in brackets are of unknown substances. The whole scheme is given in order to show the gradual loss of water of an ideal heptoxide.

The compounds $I(OH)_6(ONa)$, $OI(OH)_5$, $O_2I(OAg)_3$, and $O_3I(OAg)$ are known, corresponding to the theoretical perhalic acids. Those corresponding to the halic acids are $O_2Br(OH)$ bromic acid, and $I(OH)_5$ and $O_2I(OH)$, iodic acids. $Br(ONa)$ and $I(ONa)$, named respectively hypobromite and hypoiodite of sodium, are also known.

It may be noticed that the formulæ of some of the compounds of chromium are analogous to those of sulphur and of molybdenum; other compounds, on the contrary, show more resemblance to those of iron. While manganese, like chromium, also shows analogy with iron, it too forms $O_2Mn(OK)_2$, like $O_2S(OH)_2$ or $O_2Mo(OH)_2$, termed potassium manganate, as the others are hydrogen sulphate and hydrogen molybdate; and also MnO_2, analogous to

LiOH	$Be(OH)_2$	$B(OH)_3$	...	...	...	...	...
Li_2O	BeO	OB(OH)	$OC(OH)_2$	...	ON(OH)	...	...
...	...	B_2O_3	CO_2	$O_2N(OH)$	N_2O_3	...	OO_2
...	...	...	...	N_2O_5	...	...	...
NaOH	$Mg(OH)_2$	$Al(OH)_3$	$Si(OH)_4$	...	$P(OH)_3$	...	...
Na_2O	MgO	OAl(OH)	$OSi(OH)_2$	$OP(OH)_3$	...	...	$OS(OH)_2$
...	...	Al_2O_3	SiO_2	$O_2P(OH)$	P_2O_3	$O_2S(OH)_2$	SO_2
...	...	...	...	P_2O_5	...	SO_3	...

KOH	$Ca(OH)_2$	$Sc(OH)_3$	...	...	$As(OH)_3$	...	...
K_2O	CaO	...	$OTi(OH)_2$	$OAs(OH)_3$	OAs(OK)	...	$OSe(OH)_2$
...	...	Sc_2O_3	TiO_2	$O_2As(OH)$	As_2O_3	$O_2Se(OH)_2$	SeO_2
...	...	...	...	As_2O_5	...	...	...
RbOH	$Sr(OH)_2$	$Y(OH)_3$	...	...	$Sb(OH)_3$	...	...
Rb_2O	SrO	...	$OZr(OH)_2$	$OSb(OH)_3$	OSb(ONa)	...	$OTe(OH)_2$
...	...	Y_2O_3	ZrO_2	$O_2Sb(OH)$	Sb_2O_3	$O_2Te(OH)_2$	TeO_2
...	...	...	...	Sb_2O_5	...	TeO_3	...
CsOH	$Ba(OH)_2$	$La(OH)_3$	...	...	$Er(OH)_3$	...	...
Cs_2O	BaO	...	$OCe(OH)_2$	...	...	...	...
..	...	La_2O_3	CeO_2	...	Er_2O_3	...	...
...	...	$Yb(OH)_3$	...	...	...	...	...
...	...	...	...	...	...	...	...
...	...	Yb_2O_3	...	$O_2Bi(OH)$	$Bi(OH)_3$	...	...
...	...	...	...	Bi_2O_5	Bi_2O_3	...	...
...	...	...	$OTh(OH)_2$	...	...	...	...
...	...	...	ThO_2	...	...	...	...

...	$Zn(OH)_2$	$Ga(OH)_3$	...	...	...	...	...
Cu_2O	ZnO	...	$OGe(OH)_2$	$OV(OH)_3$	...	...	...
...	...	Ga_2O_3	GeO_2	$O_2V(OH)$	V_2O_3	$O_2Cr(OK)_2$	$CrO_2.nH_2O$
...	...	...	...	V_2O_5	...	CrO_3	CrO_2
$AgOH$	$Cd(OH)_2$	$In(OH)_3$	...	$Nb_2O_5.nH_2O$	...	$O_2Mo(OH)_2$	$MoO_2.nH_2O$
Ag_2O	CdO	In_2O_3	$SnO_2.nH_2O$	Nb_2O_5	...	MoO_3	MoO_2
...	GdO	...	TbO_2 ?	...	...	...	...
...	...	...	$OPb(OH)_2$	$Ta_2O_5.nH_2O$	...	$OW(OH)_4$	...
Au_2O	HgO	$OTl(OH)$	PbO_2	Ta_2O_5	...	$O_2W(OH)_2$	...
...	...	Tl_2O_3	...	...	...	WO_3	...
...	...	...	...	...	...	$OU(OH)_4$	$UO_2.nH_2O$
...	...	...	...	...	...	$O_2U(OH)_2$	UO_2
...	...	...	...	...	...	UO_3	...

SO_2 and MoO_2 ; but manganese also forms $O_3Mn(OK)$, termed potassium permanganate, which is analogous in formula as well as in crystalline form with potassium perchlorate, $O_3Cl(OK)$. It is convenient, however, also to include chromium and manganese in the iron group of elements.

$Cr(OH)_3$	$Mn(OH)_3$	$Fe(OH)_3$	$Ni(OH)_3$	$Co(OH)_3$
$OCr(OH)$	$OMn(OH)$	$OFe(OH)$	...	...
Cr_2O_3	Mn_2O_3	Fe_2O_3	Ni_2O_3	Co_2O_3
$Cr(OH)_2$	$Mn(OH)_2$	$Fe(OH)_2$	$Ni(OH)_2$	$Co(OH)_2$
CrO	MnO	FeO	NiO	CoO

Elements of the palladium group have a very wide range of valency ; hence they form a large group of compounds.

			OsO_4	IrO_3	
RhO_3	$O_2Ru(OK)_2$	...	$O_2Os(OH)_2$	$O_2Ir(OK)_2$	
$Rh(OH)_4$	$Ru(OH)_4$	$Pd(OH)_4$	$Os(OH)_4$	$Ir(OH)_4$	$Pt(OH)_4$
RhO_2	RuO_2	PdO_2	OsO_2	IrO_2	PtO_2
$Rh(OH)_3$	$Ru(OH)_3$	...	...	...	
Rh_2O_3	Ru_2O_3	...	Os_2O_3	Ir_2O_3	
		$Pd(OH)_2$	...	...	$Pt(OH)_2$
RhO	RuO	PdO	OsO	IrO	PtO

The **hydroxides** of **lithium, sodium, potassium, rubidium,** and **cæsium** are all soluble white compounds, melting to colourless liquids at a red heat. They do not lose water, even at the highest temperatures, hence the oxides cannot be prepared from them ; indeed, the **oxides** are produced only by the action of the metal on the hydroxide, at a high temperature ; for instance, $2NaOH + 2Na = Na_2O + H_2$. They are white, non-crystalline substances, combining at once with water to form the hydroxides $Na_2O + H_2O = 2NaOH$. The hydroxides are prepared from the carbonates by boiling a solution with slaked lime (calcium hydroxide) : $Na_2CO_3.Aq + Ca(OH)_2.Aq = 2NaOH.Aq + CaCO_3$; or by heating to redness a mixture of the carbonate with ferric oxide, when the ferrite is formed : $K_2CO_3 + Fe_2O_3 = 2KFeO_2 + CO_2$. On treatment with water, potassium ferrite is decomposed, thus : $KFeO_2 + 2H_2O.Aq = KOH.Aq + Fe(OH)_3$.

In either case, the solution of hydroxide is evaporated to dryness in an iron vessel and fused.

These hydroxides are said to be basic, for they are neutralised by acids, forming salts. Thus, with hydrochloric acid, $KOH.Aq + HCl.Aq = KCl.Aq + H_2O$, the point of neutralisation—that is, when the acid and base are present in theoretical quantity to form the salt and water —is determined by the addition of an "indicator."

Indicators.—The most important indicators are litmus, phenol-phthaleïn, and methyl-orange. Litmus is a weak acid, red in colour, the salts of which are blue. When dissolved in water, the molecule is hardly at all ionised, hence the red colour of the acid is alone visible. If a base such as sodium hydroxide is added, which, in aqueous solution, is largely ionised into $\overset{+}{Na}.Aq$ and $\overset{-}{OH}.Aq$, the hydroxyl ions combine with that portion of the hydrogen ions of the litmus acid which exist in solution; when these are withdrawn, more hydrogen ions take their place, and the solution acquires the colour of the ion of the litmus acid, viz., blue. Conversely, if an acid be added to a base in which the blue litmus ions are present, the hydrogen ions of the acid combine with the hydroxyl ions of the base, forming water, so long as any are present; after they are all in combination they convert the ion of the litmus acid into the red acid, non-ionised, and there is a marked colour-change. As the colours of the litmus acid and of its ion are both very bright, the presence of a mere trace of the indicator suffices. Phenol-phthaleïn, like litmus, is also a weak acid, that is, it is hardly ionised at all in dilute solution; the acid is colourless, but the ions are pink, hence the addition of a trace of free alkali causes the colourless solution to become pink. But this indicator gives results only with strong bases, like the hydroxides of the alkalies; with ammonium hydroxide, present in a solution of ammonia in water, it is not a good indicator, for NH_4OH is too weak a base, *i.e.* the hydroxyl and ammonium ions are present in too small amount to liberate the ions of the phenol-phthaleïn, unless much ammonium hydroxide is present in solution. Hence the presence of a trace of free ammonium hydroxide is not revealed by that indicator. Phenol-phthaleïn is therefore serviceable only with strong bases, but it may be used for weak acids. Methyl-orange, on the other hand, is a comparatively strong acid ; with a weak base it forms the ions of a salt, and it may therefore be used for weak bases like ammonium hydroxide, or for strong bases like the hydroxides of the alkali metals ; but it is too strong an acid to serve well as an indicator of excess of a weak acid, such as carbonic or acetic acid. Its colour-change is from orange to orange-pink.

Preparation of Basic Oxides.—The hydroxides of the metals of the sodium group, as already mentioned, do not lose water on heating, and the oxides, therefore, cannot be thus obtained. Neither do their carbonates lose carbon dioxide, nor their nitrates oxides of nitrogen, save at an impracticable temperature. But all other basic oxides may be prepared by heating the hydroxides, carbonates, or nitrates of the metals, and a few may be obtained by heating the sulphates. **Calcium** and **strontium oxides** are generally prepared from the carbonates, which are found as minerals, named limestone and strontianite respectively. The operation of preparing " quicklime " or calcium oxide is technically, but wrongly, called " burning." Alternate layers of lime and coal are placed in a tower of brick or stone, termed a limekiln ; the coal is set on fire, and its heat expels the carbon dioxide from the carbonate : $CaCO_3 = CaO + CO_2$. If calcium carbonate be heated in a closed vessel, however, so that the carbon dioxide does not escape, the dissociation proceeds until the amount of carbon dioxide in the vessel has reached a certain proportion, which is perfectly definite for each temperature, or until the carbon dioxide has attained a certain " concentration." The reaction then stops. But if the carbon dioxide be removed as it is formed, the reaction goes on to the end, until all carbon dioxide has escaped. The draught in the kiln removes the carbon dioxide, hence the product is calcium oxide. Strontium carbonate is causticised in the same way as limestone ; but the temperature for witherite ($BaCO_3$) is inconveniently high ; **baryta** is consequently prepared by heating the nitrate, $Ba(NO_3)_2$; it may be supposed to split into BaO and N_2O_5 ; the latter, however, decomposes even at moderate temperatures into NO_2 and O ; hence the equation is : $2Ba(NO_3)_2 = 2BaO + 4NO_2 + O_2$. These oxides are whitish-grey solids, volatile at the temperature of the electric arc, and combining with water with great rise of temperature to form **hydroxides.** The hydroxides are soluble in water—barium hydroxide most, calcium least. An aqueous solution of the former deposits crystals of a hydrate, $Ba(OH)_2.8H_2O$.

The sparing solubility of **calcium hydroxide** makes it possible to precipitate it by the addition of caustic alkali to a soluble salt of calcium, provided too much water is not present : $CaCl_2.Aq + 2NaOH.Aq = Ca(OH)_2 + 2NaCl.Aq$. Of course, a saturated solution of calcium hydroxide remains, hence the precipitation is not complete. This plan is applicable to the preparation of all hydroxides which are insoluble in water, unless they dissolve in excess of the caustic alkali ; if they do, they are said to display "acid" properties. Beryllium and magnesium hydroxides are thus precipitated : $MgCl_2.Aq + 2KOH.Aq = Mg(OH)_2 + 2KCl.Aq$. The hydroxide may be filtered off and dried, and the white mass, on ignition, leaves the oxide as a white powder. By this means, too, the **hydroxides** of **copper** (cupric, $Cu(OH)_2$), **silver,** AgOH, **zinc,** $Zn(OH)_2$, **cadmium,** $Cd(OH)_2$, **aluminium,** $Al(OH)_3$, **scandium, yttrium, lanthanum,** and **ytterbium, gallium, indium,** and **thallium,** with similar formulæ, **titanium, zirconium, thorium,** with formulæ $OM(OH)_2$, (where M stands for an element of that group ; **germanium, tin** (stannous, $Sn(OH)_2$, and stannic, $SnO_2.nH_2O$), **lead** (plumbous, $Pb(OH)_2$), **bismuthous,** $Bi(OH)_3$, **chromic,** $Cr(OH)_3$, and **chromous,**

$Cr(OH)_2$, **manganic** and **manganous**, **ferric** and **ferrous**, **cobaltous** and **nickelous**: in short, from all elements which form "basic" hydroxides. And from almost all these the **oxides** may be obtained by heating the hydrates to redness. Excess of the precipitant, however, must be avoided in many cases, for some of these hydroxides display acid properties if in presence of excess of alkali. Thus, for example, if excess of sodium hydroxide or potassium hydroxide be added to the solution of a soluble salt of zinc, such as the chloride, nitrate, or sulphate, the first change, as already shown, is the precipitation of the hydroxide; but on addition of excess of alkali, the precipitate redissolves, forming the compound $Zn(OK)_2.Aq$, of which the ions are $\overset{+}{K}$, $\overset{+}{K}$, and $\overset{-\;-}{Zn}O_2$; this compound is thrown down by alcohol, in which it is insoluble. It is generally named **zincate** of **potassium.** **Cadmium** forms a similar compound, but that of **aluminium** has the formula $OAl(OK)$; the hydroxide, $Al(OH)_3$, on losing water is transformed into the condensed hydroxide, $OAl(OH)$, which may be termed **aluminic acid,** of which the hydrogen atom is exchangeable for metals. **Stannous** and **plumbous** hydroxides dissolve in excess of alkali, doubtless forming compounds similar to that of zinc; and **chromic** hydroxide is soluble in cold solution of caustic alkali, forming, no doubt, a compound analogous to that of aluminium; but it is decomposed on warming, with reprecipitation of the hydroxide. The hydroxides of all these elements may also be precipitated by a solution of ammonium hydroxide, and some of them are redissolved; but the compounds formed are of a different nature from those described in the case of zinc, &c., and will be afterwards considered.

Properties of the Hydroxides.—As regards the properties of the hydroxides, that of copper (cupric) is light blue, and of silver, brown; chromic hydroxide is grey-green, and chromous, yellowish; manganic, brown, and manganous, very pale pink; ferric, rust brown, and ferrous, white when pure, but usually dirty green; cobaltous, dingy red, and nickelous, grass-green. The others are all white amorphous bodies, and they all yield oxides on heating. Cupric oxide is black; even when boiled with water the hydroxide loses water and changes colour. Argentous oxide is brown; when heated to redness it loses oxygen, leaving a residue of metallic silver. Zinc oxide is yellow when hot and white when cold; cadmium oxide is a brown powder; the oxides of aluminium, scandium, yttrium, lanthanum, ytterbium, gallium, and indium, and of titanium, zirconium, thorium, germanium, and stannic oxide are white powders; thallium oxide is a yellow powder; tin monoxide is a black powder; that of lead (litharge, massicot) is a yellow substance, fusible at a red heat; bismuth sesquioxide is a yellowish powder; chromic, ferric, and manganic are respectively green, rust-red, and brown; chromous oxide is unknown, for any attempt to dry it results in the decomposition of water, the absorption of its oxygen by the chromous oxide which becomes chromic oxide, and the evolution of hydrogen. Ferrous hydroxide can be dried, but only with rigid exclusion of air; it is a black powder. Manganous oxide is greyish-green, cobaltous, olive-green, and nickelous also greyish-green. Manganous hydroxide must also be dried in absence of air.

These hydroxides and oxides are named bases. There are some basic oxides, which are precipitated by adding a hydroxide, such as that of sodium, to a soluble salt, and to which there is no corresponding hydroxide. This is the case with the oxides of mercury. On referring to the table of halides on p. 50, it will be seen that the chloride of mercury has the formula $HgCl_2$. This compound, commonly called corrosive sublimate, when treated in solution with sodium hydroxide, gives a precipitate, not of hydroxide, as might be expected, but of oxide: $HgCl_2.Aq + 2NaOH.Aq = HgO + 2NaCl.Aq + H_2O$. Similarly, a soluble mercurous salt, such as mercurous nitrate, $Hg_2(NO_3)_2$, on treatment with an alkali gives a precipitate of mercurous oxide: $Hg_2(NO_3)_2.Aq + 2NaOH.Aq = Hg_2O + 2NaNO_3.Aq + H_2O$. These are cases of relative stability; for, as has been already remarked, on boiling a solution from which cupric hydroxide has been precipitated, the blue hydroxide is changed into black oxide; other hydroxides lose their water at a still higher temperature; while those of the alkaline metals may be volatilised without decomposing.

Oxides produced by Heating Carbonates.—Most of the basic oxides may also be prepared by heating the carbonates, a class of salts afterwards to be discussed. The carbonates of the alkali metals, however, are not thus decomposed; like their hydroxides, they may be volatilised without decomposition. But all other carbonates are decomposed by exposure to a red heat. The process has already been described as a method of manufacturing quicklime. Most carbonates, however, do not require the same high temperature; a dull red heat suffices. And the oxides do not, as a rule, recombine with the carbon dioxide expelled, as does lime; hence there is no danger of re-carbonating the oxide.

Oxides produced by Heating Nitrates.—The nitrates, too, of nearly all the basic metals, yield the respective oxides when they are heated to bright redness. The nitrates of the alkali metals in this instance, as in others, do not behave in this way. When heated they lose oxygen, but only at a very high temperature, forming the nitrites, a class of salts afterwards to be described. Thus, potassium nitrate undergoes the decomposition: $2KNO_3 = 2KNO_2 + O_2$. The product of heating the other nitrates, however, is the oxide, while a mixture of oxides of nitrogen is evolved. This may be supposed to take place in two stages: first, the nitrate may be imagined to decompose into the oxide and nitrogen pentoxide, thus: $Zn(NO_3)_2 = ZnO + N_2O_5$; the last compound is very easily decomposed by heat, and yields a lower oxide of nitrogen: $2N_2O_5 = 4NO_2 + O_2$; while if the temperature is over 600°, which is usually exceeded in decomposing the nitrates, the nitric peroxide is partly further decomposed into nitric oxide and oxygen: $2NO_2 = 2NO + O_2$. The products, therefore, are NO_2, NO, and O_2.

A metal which forms two oxides, one containing more oxygen than the other, if the nitrate of the lower oxide is heated, yields the higher oxide. Cases of this are mercury, tin, and iron. Mercurous nitrate, carefully heated, gives, not mercurous oxide, Hg_2O, but mercuric oxide, HgO: $HgNO_3 = HgO + NO_2$; similarly $Sn(NO_3)_2$ yields SnO_2, and not SnO; and $Fe(NO_3)_2$, Fe_2O_3, and not FeO.

Oxides produced by Heating Sulphates.—The sulphates require a higher temperature than the nitrates for their decomposition, consequently they are not generally used as a source of oxides. But the equivalents of magnesium, zinc, and some other metals have been determined by estimating the weight of oxide obtainable on heating a weighed amount of sulphate; and ferrous sulphate has been distilled in fireclay retorts for many years past at Nordhausen, in Saxony, for the purpose of making "Nordhausen sulphuric acid," $H_2S_2O_7$, and red oxide of iron, Fe_2O_3, which, made in this way, has a fine colour, and is used as a paint. When a sulphate is heated, the gas which escapes is not entirely SO_3, as might be imagined from the equation: $MgSO_4 = MgO + SO_3$; the high temperature decomposes most of the sulphur trioxide into the dioxide, SO_2, and oxygen; and the oxygen, in the case of ferrous sulphate, oxidises the FeO into Fe_2O_3.

Sulphides and Hydrosulphides.—The analogy between the elements oxygen and sulphur is well shown by comparing the **sulphides** of the elements of which the oxides have been described. Elements of the **lithium** group form both **hydrosulphides** and **sulphides**; thus we know **sodium hydrosulphide**, NaSH, analogous to the hydroxide NaOH, and **sulphide**, similar in formula to the oxide Na_2O, Na_2S. Hydrogen sulphide is a weak acid; hence, on passing hydrogen sulphide through a concentrated solution of sodium hydroxide at 95° until saturation is complete, white crystals of $NaSH.2H_2O$ deposit on evaporation. The equation is: $\overset{+}{Na}\overset{-}{OH}.Aq + \overset{+}{H}\overset{-}{SH}.Aq = \overset{+}{Na}\overset{-}{SH}.Aq + H_2O$. On mixing the solution with an equivalent quantity of sodium hydroxide and evaporating, the sulphide is produced: $\overset{+}{Na}\,\overset{-}{SH}.Aq + \overset{+}{Na}\overset{-}{OH}.Aq = \overset{+}{Na_2}\overset{--}{S}.Aq + H_2O$. Here it must be supposed that the hydrogen of the hydrosulphide is present as an anion, and that it reacts with the hydroxyl of the caustic soda, forming water, while the sodium sulphide remains in solution in an ionised form, and can be recovered on evaporation in crystals with $9H_2O$. Similar compounds exist with potassium.

Calcium, **strontium**, and **barium** also form **hydrosulphides** and **sulphides**, analogous in formula to the hydroxides and oxides. They are similarly prepared to the sodium compounds, but, as the metals are dyads, their formulæ are $M(SH)_2$ and MS; and there is an intermediate compound between the hydroxide and hydrosulphide, having, in the case of calcium, the formula $HSCaOH$. They are also soluble in water. **Magnesium**, too, forms a **hydrosulphide**, probably $Mg(SH)_2$; it is prepared by passing sulphuretted hydrogen into water in which magnesium oxide is suspended. It is unlike the hydrosulphides of the alkalies, for while they do not decompose with water, it, on the contrary, when its solution is heated to 80°, reacts with water, yielding hydroxide and sulphuretted hydrogen: $Mg(SH)_2.Aq + 2HOH = Mg(OH)_2 + 2H_2S$. The probable explanation of this change is that water is not wholly non-ionised, but that there are present some hydrogen ions; these are not so inconsiderable in number, compared with those of the weak acid H_2S; on raising temperature, a certain amount of hydrogen sulphide is liberated, and, being volatile, it escapes, and is no longer present to act on the magnesium hydroxide and reconvert it into sulphide.

Sulphides of **boron**, **aluminium**, **chromium**, and **silicon** are at once decomposed by water, and cannot, therefore, be produced in aqueous solution. They are white substances formed by heating the elements to a high temperature in a current of sulphur vapour.

The **sulphides** of **copper**, **silver**, **gold**, **cadmium**, **mercury**, **indium**, **thallium**, **tin**, **lead**, **arsenic**, **antimony**, and **bismuth**, and of the metals of the **palladium** and **platinum** groups, are all insoluble in water, or, to be more accurate, very sparingly soluble. They form no hydrosulphides. Hence they are precipitated from soluble salts of these metals by addition of sulphuretted hydrogen; they form flocculent precipitates, usually characterised by striking colours, and are therefore generally used as a means of recognising the metal. CuS, Ag_2S, Au_2S_3, HgS, Tl_2S, Tl_2S_3, PbS, PtS_2, and the other sulphides of the platinum group of metals are black; CdS, SnS_2, and As_2S_3 are yellow; In_2S_3, SnS, and Bi_2S_3 are brown, and Sb_2S_3 is orange. These sulphides are not attacked by dilute acids. On the other hand, the sulphides of zinc, manganese, iron, cobalt, and nickel are not precipitated by hydrogen sulphide, but they are thrown down by a soluble sulphide or hydrosulphide, such as those of ammonium or sodium. They, too, form flocculent precipitates; ZnS is white, MnS pink, and FeS, CoS, and NiS are black. The reason of the difference in the behaviour of the two classes of sulphides is an interesting one, and will be now explained.

Solubility-Product.—It has already been mentioned on p. 14 that the rate of chemical change depends on the amount of each of the reacting substances present in unit volume. This last is generally termed the "concentration" of these substances, for the more concentrated the solution the greater the mass present in unit volume. Now, if two kinds of ions, such as $\overset{+}{Na}$ and $\overset{-}{Cl}$, are present in solution, necessarily in equal numbers, the solution will also contain a certain number of molecules of non-ionised NaCl, formed by their union, and the relative number of ions and molecules will depend on the concentration; the number of ions in proportion to the number of non-ionised molecules will be greater, the greater the dilution. For each dilution (and for each temperature) a state of balance will result; the position of this equilibrium will depend on the relative rate at which ionisation and union of ions to form molecules go on; if ionisation takes place twice as quickly as combinations of ions to form molecules, then two-thirds of the dissolved substance will exist as ions, the remaining third being non-ionised molecules. If the solution is made more concentrated by evaporation, the conditions are changed, and the rate of ionisation is reduced compared with the rate of union of ions with each other. Suppose that concentration be pushed so far that solid salt separates out; the limit of concentration will be reached, since it is now impossible to alter the number of ions and of molecules in unit volume of the solution. The ratio will now remain constant, and if c and c' be the concentrations of the ions (and they are, of course, equal), and if C be that of the non-ionised molecules, then $c.c' = k.C$, k being a factor expressing the relative proportions of the non-ionised molecules. If k is very small, then there are many molecules and few ions present; if, on the contrary, k is large, the ions are numerous and the molecules few. The expression $k.C$ is termed the "solubility-product."

To take a specific case:—A solution of ammonia in water consists partly of the ions NH_4 and OH, and partly of non-ionised molecules of NH_4OH; it is a weak base—that is, the number of non-ionised molecules is much greater than that of the ions. In a solution containing 1.7 grams of ammonia per litre (one-tenth normal solution), only 1.5 per cent. of the total number of molecules exist in the ionic state. Hence a solution of ammonia, unlike one of caustic soda or potash, gives no precipitate of hydroxide when added to a solution of salts of the relatively strong bases, such as calcium, strontium, or barium chlorides. With salts of the weaker base magnesia, however, ammonia produces a precipitate of magnesium hydroxide. It is possible still further to reduce the ionisation of ammonia solution; this can be done by the addition of an ammonium salt, such as the chloride, which, like most such salts, is highly ionised. The reason is, that while (concentration of $\overset{+}{\mathrm{NH}_4}$) × (concentration of $\overset{-}{\mathrm{OH}}$) = k × (concentration of $\mathrm{NH_4OH}$), if more ammonium ions be added, the number of hydroxl ions will diminish by union with $\mathrm{NH_4}$ ions, forming non-ionised ammonium hydroxide, because the increase of the number of ammonium ions will increase the value of the product on the left-hand side of the equation, and in order that it may balance that of the right, the relative number of molecules of $\mathrm{NH_4OH}$ must be increased; and we may see that if ammonium chloride is added to a solution of magnesium chloride, ammonia solution will no longer produce a precipitate of magnesium hydroxide; the ammonia is too weak a base, that is, it contains too few hydroxyl ions, which are the reason of its basic nature.

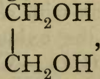
Let us now return to the consideration of the insolubility of sulphides of the copper group in acids and the solubility of such sulphides as that of zinc. No substance, as has been before remarked, is wholly insoluble in water; zinc sulphide, however, belongs to the very sparingly soluble compounds. Hence the product $c(\overset{++}{\mathrm{Zn}}) \times c'(\overset{--}{\mathrm{S}})$ has a very small value, for it is equal to $k.C(\mathrm{ZnS})$, which must necessarily be very small, seeing that the compound is so sparingly soluble. Now, the ions of $\mathrm{H_2S}$ are $\overset{+}{\mathrm{H}}$, $\overset{+}{\mathrm{H}}$, and $\overset{--}{\mathrm{S}}$; but though the ionisation is very small, hydrogen sulphide being a very weak acid, they are yet sufficient to reach the value of the very small solubility-product $k.C(\mathrm{ZnS})$. If, however, the concentration of the $\overset{--}{\mathrm{S}}$-ions is still further diminished by addition of some compound rich in $\overset{+}{\mathrm{H}}$-ions, such as $\overset{+}{\mathrm{H}}\overset{-}{\mathrm{Cl}}$.Aq, then the product $c(\overset{++}{\mathrm{Zn}}) \times c'(\overset{--}{\mathrm{S}})$ will be less than $k.C(\mathrm{ZnS})$, and there will be no precipitate; or if hydrochloric acid be added to precipitated zinc sulphide, it will be dissolved. On the other hand, the addition of acetic acid, a weak acid, and poor in hydrogen ions, does not bring about solution of zinc sulphide; indeed, the precipitation of zinc from a solution of its acetate by hydrogen sulphide is almost complete.

The solubility-product of copper sulphide, and of the other sulphides which are not soluble in dilute acids, is still less; hence hydrogen sulphide precipitates them from acid solution, for the concentration of the $\overset{--}{\mathrm{S}}$-ions of the hydrogen sulphide may be very much diminished without the product $c(\overset{++}{\mathrm{Cu}}) \times c'(\overset{--}{\mathrm{S}})$ becoming less than $k.C(\mathrm{CuS})$, for CuS is still less soluble in water than ZnS.

Oxides and Hydroxides of Complex Groups. —The oxides and hydroxides of complex groups show analogy in their formulæ, and often in their methods of preparation with the basic oxides and hydroxides. A few instances of these will now be given.

Ammonia (see p. 42) is very soluble in water; at the ordinary temperature, no less than 800 volumes of the gas dissolve in one volume of water, forming a very pungently smelling solution named *liquor ammoniæ.* This solution consists for the most part of a mixture of liquid ammonia with water; it probably also contains **ammonium hydroxide,** $\mathrm{NH_4OH}$, and, as already mentioned, less than 1.5 per cent. of the ions $\overset{+}{\mathrm{NH_4}}$ and $\overset{-}{\mathrm{OH}}$. It is, therefore, a weak base.

Hydrazine, $\mathrm{N_2H_4}$, also forms a **hydrate,** $\mathrm{N_2H_5OH}$, a fuming liquid with slight smell (and consequently in all probability fairly highly ionised); it boils at 119°, and is very corrosive, attacking wood, cork, and even glass. It has a strong reducing action, so that if added to a solution of cupric sulphate which contains cupric ions, $\overset{++}{Cu}$, it gives an immediate precipitate of cuprous oxide, Cu_2O, nitrogen being evolved. Like ammonia, it precipitates such hydroxides as that of aluminium, iron, &c. **Hydroxylamine,** NH_2OH, is a somewhat similar body, produced by passing nitric oxide, NO (see p. 97), through a mixture of granulated tin and hydrochloric acid, to which a little platinic chloride has been added ; the nascent hydrogen reduces the nitric oxide to hydroxylamine ; it unites with the hydrochloric acid, forming hydroxylamine hydrochloride, NH_3OHCl. After removal of the tin by addition of sodium hydroxide and filtration, the solution is evaporated to dryness and mixed with alcohol ; hydroxylamine hydrochloride dissolves, while sodium chloride remains. A solution of the base may be obtained by addition of silver hydroxide : $NH_3OHCl.Aq + AgOH.Aq = AgCl + NH_3OH.Aq$. If sodium methoxide (see p. 88) be added to a solution of the hydrochloride in methyl alcohol, the base is liberated, and can be separated from the alcohol by fractional distillation ; it is a volatile white solid. This compound is interesting, because the OH group is under no circumstances an ion ; its solution in water must contain ions of $\overset{+}{NH_3OH}$ and $\overset{-}{OH}$, since it reacts like ammonium hydroxide.

Alcohols.—The **hydroxides** of the **hydrocarbon radicles** are, as mentioned on p. 67, termed **alcohols.**[1] Of these there are very many, but a few only will be chosen to serve as examples : **methyl alcohol,** CH_3OH, **ethyl alcohol,** $CH_3–CH_2OH$, as types of monohydric alcohols, which may be taken as the analogues of the hydroxides of the monad metals ; **glycol,**  $\begin{array}{c}CH_2OH\\ |\\ CH_2OH\end{array}$, a dihydric alcohol, may be likened to barium hydroxide,

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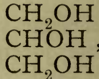
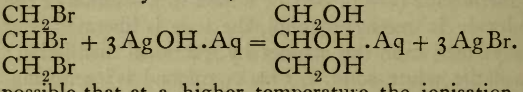
[1] A special class of such hydroxides derived from benzene, C_6H_6, are termed phenols. "Carbolic acid," C_6H_5OH, is the best known of these.

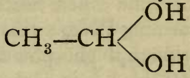
$Ba(OH)_2$; and glycerine (glycerol),  $\begin{array}{l}CH_2OH\\ CHOH\\ CH_2OH\end{array}$, is a trihydric alcohol, as aluminium hydroxide is a trihydroxide. These substances differ from the hydroxides, however, by their being non-electrolytes, and therefore non-ionised. Or perhaps it is more correct to say that their conductivity is of the same order of magnitude, but less in value, than that of pure water. The corresponding halides, for example, CH_3Cl, $C_2H_4Cl_2$, and $C_3H_5Cl_3$, are also regarded as non-ionised; they are practically insoluble in water. Nevertheless, methyl chloride has been transformed into methyl alcohol by heating with water to a high temperature in a sealed tube under pressure—$CH_3Cl + HOH = CH_3OH + HCl$; and the others, but preferably the bromides, may be similarly changed into hydroxides by heating with silver hydroxide, or with silver oxide and water:

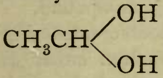


$$\begin{array}{l}CH_2Br\\ CHBr\\ CH_2Br\end{array} + 3AgOH.Aq = \begin{array}{l}CH_2OH\\ CHOH\\ CH_2OH\end{array}.Aq + 3AgBr.$$

Is it possible that at a higher temperature the ionisation is sufficient (though it must be exceedingly small) to produce the interaction?

The metals sodium and potassium dissolve in the alcohols, with evolution of hydrogen, forming compounds somewhat analogous to the hydroxides; instead of hydrogen, however, they contain a hydrocarbon group: **sodium methoxide**, for example, has the formula $Na(OCH_3)$. Such substances are white solids, like caustic soda.

Aldehydes.—The alcohols, if oxidised by boiling them with chromic acid, yield a class of bodies analogous to the oxides, termed **aldehydes**: $CH_3{-}CH_2{-}OH + O = (CH_3 - CH)''O + H_2O$. It will be noticed that ethane, $CH_3 - CH_3$, has lost two hydrogen atoms, and that the residue, $CH_3 - CH_2$, is now a dyad group, capable of combination with an atom of dyad oxygen. The aldehydes are volatile liquids, with strong odour, and those containing few atoms of carbon are miscible with water. They form easily decomposable compounds with water, which are di-hydroxides; *e.g.* ordinary aldehyde forms  $CH_3{-}CH\begin{smallmatrix}OH\\OH\end{smallmatrix}$; they are called **aldehydrols.** When brought into contact with solutions from which hydrogen is being evolved, the aldehydrols lose oxygen, and are converted into alcohols:



$$CH_3CH\begin{smallmatrix}OH\\OH\end{smallmatrix} + 2H = CH_3{-}CH_2OH + H_2O.$$

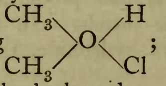
The alcohols cannot be termed basic substances; still, it is evident that they show analogy with the true bases in many respects.

Amines and Phosphines.—Derivatives of nitrogen, phosphorus, sulphur, and even of iodine and of oxygen, containing hydrocarbon groups, are however known, which are true bases, though weak ones. If ammonia in alcoholic solution be heated with excess of methyl iodide, **tetra-methyl-ammonium iodide** is formed: $NH_3 + 4CH_3I = N(CH_3)_4I + 3HI$. This iodide, digested with water and silver hydroxide, exchanges iodine for hydroxyl, and after removal of the silver iodide by filtration the solution may be evaporated to dryness. The residue is a white solid, of the formula $N(CH_3)_4OH$; it is termed **tetra-methyl-ammonium-hydroxide**; in its reactions it shows great analogy with caustic potash, having a caustic taste, and producing precipitates with the usual salts of the metals. In solution it is more ionised than ammonium hydroxide, though less than that of potassium.

Phosphine, as remarked on p. 66, combines with hydrogen iodide, forming a salt, PH_4I, phosphonium iodide, resembling ammonium chloride. But as it is decomposed by water into phosphine, PH_3, and hydrogen iodide, an attempt to convert it into phosphonium hydroxide, PH_4OH, cannot be made. Substituted phosphonium compounds, however, are known, in which a hydrocarbon radicle, such as methyl, replaces hydrogen. Sodium and phosphorus combine when heated together under an oil called xylene, forming PNa_3; this body, treated with methyl iodide, yields trimethyl phosphine, $P(CH_3)_3$; with more methyl iodide $P(CH_3)_4I$ is formed; and its solution in water, which is not decomposed by the solvent, yields with silver hydroxide **tetra-methyl-phosphonium hydroxide,** $P(CH_3)_4OH$, a base resembling the corresponding ammonium compound.

These compounds exist owing to the double valency of nitrogen and of phosphorus, which can function either as triad or pentad. Double valency is to be noticed also with oxygen and with sulphur, although with the former tetrad combinations are far from stable, while with the latter both dyad and tetrad compounds can be formed.

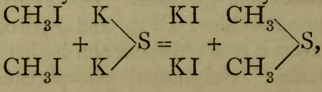
Ethers.**—Oxide** of **methyl** and **oxide** of **ethyl,** which are usually named methyl and ethyl ethers, are formed by mixing solutions in alcohol of methyl or ethyl iodide with sodium methoxide or ethoxide: $CH_3I.Alc + NaOCH_3.Alc = NaI + H_3COCH_3.Alc$. The ether has a low boiling-point, and can be separated by fractional distillation from the alcohol in which it is dissolved. Methyl ether is a gas; ethyl ether a volatile liquid, boiling at 37°. Such compounds can also be prepared more readily by distilling a mixture of the alcohol with sulphuric acid, which yields HCH_3SO_4, hydrogen methyl sulphate, with the alcohol: $HCH_3SO_4 + CH_3OH = H_3COCH_3 + H_2SO_4$. Now, methyl ether and hydrochloric acid combine at a low temperature, yielding



$$\begin{matrix}CH_3\\ CH_3\end{matrix}\!>O<\!\begin{matrix}H\\ Cl\end{matrix}$$

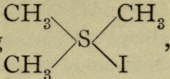
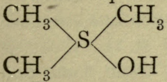
; but it is impossible to replace the chlorine by hydroxyl.

Similar sulphur compounds, however, are stable. Methyl sulphide, produced by the action of methyl iodide on potassium sulphide,



$$\begin{matrix}CH_3I\\ CH_3I\end{matrix} + \begin{matrix}K\\ K\end{matrix}\!>S = \begin{matrix}KI\\ KI\end{matrix} + \begin{matrix}CH_3\\ CH_3\end{matrix}\!>S,$$

unites with

methyl iodide, forming , a compound containing tetrad sulphur; with silver hydroxide it yields the corresponding **tri-methyl-sulphonium hydroxide,** , a compound exhibiting basic properties.

From iodine, too, **iodonium compounds** have been prepared, in which the iodine functions as a triad; and a hydroxide with basic properties is known.

CHAPTER V

Neutral Oxides—Peroxides—Action of Nitric Acid on Metals; on Oxidisable Substances—Complexity of Oxides—Spinels and Similar Compounds.

THE properties of all chemical compounds show gradation; and there is a slow transition from basic oxides and hydroxides, like those which we have been considering in the last chapter, to acid oxides and hydroxides. The transition takes place along two paths; first, there are some oxides which are neither basic nor acid; and second, a number of oxides exist which are either basic or acid, according to circumstances. We shall consider first the neutral oxides.

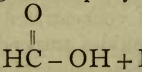
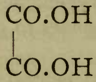
Peroxides.—In the potassium and calcium groups of elements, peroxides are known. When sodium is burned in air a light yellow powder is formed, **sodium dioxide,** of the formula Na_2O_2; **potassium** yields a **tetroxide,** K_2O_4. Both of these substances react with water, giving off oxygen; but if they are very slowly added to the water, so that the temperature does not rise much, a solution is obtained. The corresponding **barium** compound is formed when barium monoxide is heated under pressure in air (see p. 13). On addition to water it forms a hydrate, probably $Ba{=}O(OH)_2.7H_2O$. On treatment with acid, **hydrogen dioxide,** H_2O_2, is formed; and if sulphuric acid be added in theoretical amount to the barium dioxide, nearly insoluble barium sulphate is formed, along with a fairly pure solution of hydrogen dioxide: $BaO{=}(OH)_2.Aq$

$+ H_2SO_4.Aq = BaSO_4 + O{=}OH_2.Aq$. It can be purified, and indeed obtained anhydrous by distillation under very low pressure. It then forms a somewhat viscous, colourless liquid, with a sharp taste.

There is some doubt as to the constitution of hydrogen dioxide, and consequently of the dioxides from which it is derived. It is unlikely that barium ever acts as a tetrad, and much more probable that this character is to be attributed to oxygen; hence the formula of its dioxide is more likely to be $Ba{=}O{=}O$, than $O{=}Ba{=}O$; and consequently hydrogen dioxide has more probably the formula $O{=}OH_2$, than $HO{=}OH$. Indeed, hydrogen dioxide is possibly a weak acid, since the hydrated **dioxides** of **calcium** and **barium** are precipitated on addition of concentrated solutions of hydrogen dioxide to the hydroxides suspended in water. These substances have all bleaching power, for they readily part with their second atom of oxygen, and it is capable of oxidising coloured insoluble substances to colourless soluble ones.

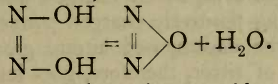
Neutral Oxides, Class I.—The next neutral oxides met with are **carbon monoxide,** CO, **nitrous oxide,** N^2O, and **nitric oxide,** NO. These are all gases, but condense at low temperatures to colourless liquids, and at still lower, freeze to white solids.

Carbon monoxide is prepared by burning carbon in a supply of oxygen insufficient to convert it into the dioxide; or by passing the dioxide over a layer of carbon, heated to redness. It appears that the monoxide is always the first product; for if moisture be excluded during the combustion of carbon in oxygen, the amount of dioxide relatively to the monoxide is very small; and it is known that if water-vapour be absent, carbon monoxide cannot be induced to explode with oxygen. If even the minutest amount of moisture be present, on passing a spark the union takes place with explosion. This phenomenon is not easily accounted for; it is readily represented by the equation $2CO + H_2O + O_2 = 2CO_2 + H_2O$. Can it be that at the very low pressure of the water-vapour a trace is ionised into $\overset{+}{H}$ and $\overset{-}{OH}$, and that the $\overset{-}{OH}$ furnishes the oxygen for the CO, the hydrogen recombining with oxygen to re-form the molecule of water? For it has been found that no moisture is requisite to promote the union of oxygen and hydrogen if these gases be heated together. Phosphorus and sulphur, too, show reluctance in uniting with oxygen, in absence of moisture. In ordinary moist air, carbon monoxide burns with a blue flame. It is nearly insoluble in and has no action on water.

Other methods of preparing carbon monoxide are: by withdrawing the elements of water from formic acid by adding it drop by drop to warm concentrated sulphuric acid;  $H\overset{\overset{O}{\|}}{C}-OH + H_2SO_4 = CO + H_2SO_4.H_2O$; by heating a mixture of oxalic acid with concentrated sulphuric acid;  $\begin{array}{l}CO.OH\\ |\\ CO.OH\end{array} + H_2SO_4 = CO + CO_2 + H_2SO_4.H_2O$; the carbon dioxide is separated from the monoxide by bubbling the mixture of gases through a solution of caustic potash, which absorbs the dioxide, allowing the monoxide to pass; and lastly, by heating a mixture of potassium ferrocyanide and fairly concentrated sulphuric acid; $K_4Fe(CN)_6 + 6H_2SO_4 + 6H_2O = 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO$. In the last reaction, it may be taken that hydrocyanic acid, HCN, is first liberated, and that it reacts with water, forming ammonia and carbon monoxide: $HCN + H_2O = NH_3 + CO$; the ammonia subsequently combines with the sulphuric acid.

If carbon monoxide is passed over metallic nickel or iron in a fine state of subdivision produced by reducing their oxides, volatile compounds are formed of the formulæ $Ni(CO)_4$, and $Fe(CO)_5$; on exposing the latter to light gold-coloured crystals are formed, of the formula $Fe_2(CO)_7$. The **nickel carbonyl** boils at 43°, and the **iron pentacarbonyl** at 103°; **di-ferro-hepta-carbonyl** decomposes when even moderately heated. At 180° these compounds are decomposed into metal and carbon monoxide, the metal being deposited as a mirror on the hot surface.

Nitrous oxide, N_2O, is most readily prepared by heating ammonium nitrate, NH_4NO_3; the equation is: $NH_4NO_3 = N_2O + 2H_2O$. It is somewhat soluble in water, and is best collected by downward displacement. The aqueous solution has a sweetish taste; and the gas, if breathed, produces insensibility; it is therefore frequently employed by dentists as an anæsthetic. If a mixture with air is respired, it produces with some persons a state of excitement, which has procured for it the name "laughing-gas." It is an endothermic compound, and if submitted to sudden shock it explodes with violence. It may be supposed that the fulminate used to explode it decomposes some molecules in the neighbourhood; these, on decomposing, evolve heat, and decompose their neighbours, and the explosion rapidly travels throughout the gas; the products are nitrogen and oxygen. A candle will burn in nitrous oxide, for the temperature of the flame is sufficiently high to decompose the gas, and the combustion proceeds as in dilute oxygen. Although nitrous oxide is not acted on by water or bases it has claims to be regarded as the anhydride of hyponitrous acid, from a solution of which it is liberated by heat:



$$\begin{array}{c} N-OH \\ \| \\ N-OH \end{array} = \begin{array}{c} N \\ \| \\ N \end{array}\!\!>O + H_2O.$$

As neither ammonium nitrate nor hyponitrous acid can be reproduced by bringing together nitrous oxide and water, its production by heating one of these compounds is termed an "irreversible reaction."

Action of Nitric Acid on Metals.—The product of the action of nitric acid on metals varies according to the metal acted on, the concentration of the acid, and the temperature. The acid in aqueous solution is more or less ionised, the ions being $\overset{+}{H}$ and $\overset{-}{NO_3}$. If a metal of which the ions are highly electropositive is presented to these ions of nitric acid the hydrogen ions impart their charge to the non-ionised metal, which metal enters into solution as ions, while hydrogen is evolved. This is the case when nitric acid acts on magnesium, and theoretically also on aluminium, manganese, zinc, cadmium, iron, cobalt, and nickel, for all these metals in the ionic state have higher electro-affinity than hydrogen, and that in the order given. It may be termed the normal action of acids on metals, and represented thus: $M + 2\overset{-}{H} = \overset{++}{M} + H_2$. But along with this action others take place in which the nitric ion is "reduced" or deprived of oxygen. Some examples of this will now be given.

When **silver** is attacked by nitric acid, **nitric peroxide**, NO_2, is produced, and partly evolved as gas. The reacting substances are Ag, and $\begin{matrix}\overset{+}{H}\\+\\H\end{matrix}$ and $\begin{matrix}\overset{-}{NO_3}\\-\\NO_3\end{matrix}$; one of the $\overset{-}{NO_3}$ groups loses oxygen, being converted into electrically neutral NO_2 and an ion of oxygen, $\overset{--}{O}$, which combines with the two hydrogen ions, forming water, non-ionised, H_2O. But this leaves a negatively charged nitrate group without a corresponding positively charged partner; moreover, the charge of the decomposed nitrate group is still available. An atom of silver, therefore, goes into solution as a positively charged ion, and restores electric equilibrium in the solution. With less concentrated acid the nitrate ion parts with two atoms of oxygen, requiring three negative electrons, in addition to the one originally attached to the group $\overset{-}{NO_3}$; to effect this three positive electrons must attach themselves to three atoms of silver, which then go into solution as ions, hence the charge is: $3Ag + 4\overset{+}{H} + 4\overset{-}{NO_3} = NO + 2H_2O + 3\overset{+}{Ag} + 3\overset{-}{NO_3}$, the balance of electric charge not having been disturbed, although one negative and one positive electron have disappeared. With metals yielding kations of higher potential, the reduction of the nitrate ion goes still farther; nitrous oxide, N_2O, nitrogen, and even ammonia may be produced, in relative amounts depending on the metal, on the concentration, and on the temperature. It may be taken that the lower the temperature, the less the concentration, and the higher the metal stands in the electro-negative series, the greater the reduction. The equations are: $4M'' + 10\overset{+}{H} + 10\overset{-}{NO_3} = N_2O + 5H_2O + 4\overset{++}{M} + 8\overset{-}{NO_3}$; $5M'' + 12\overset{+}{H} + 12\overset{-}{NO_3} = N_2 + 6H_2O + 5\overset{++}{M} + 10\overset{-}{NO_3}$; $4M'' + 10\overset{+}{H} + 10\overset{-}{NO_3} = \overset{+}{NH_4} + 4\overset{++}{M} + 9\overset{-}{NO_3} + 3H_2O$. All these changes may proceed simultaneously; but **copper** and moderately strong nitric acid yields fairly pure **nitric oxide**; if more concentrated acid be employed, a mixture of varying proportions of nitric oxide and peroxide are evolved; while by using **zinc** or **magnesium** and very dilute acid, **nitrous oxide, nitrogen, hydrogen**, and **ammonium nitrate** are the main products.

Oxidation by means of Nitric Acid.—Action of the same nature occurs when an element capable of changing its valency, *i.e.* the number of electrons associated with its ionised atom, is treated in the ionic condition with nitric acid. For example, the ferrous ion, $\overset{++}{Fe}$, on treatment with nitric acid at 100° becomes ferric, $\overset{+++}{Fe}$, while nitric oxide is evolved: $3\overset{++}{Fe} + 6\overset{-}{R} + 4\overset{+}{H} + 4\overset{-}{NO_3} = NO + 2H_2O + 3\overset{+++}{Fe} + 3\overset{-}{NO_3} + 6\overset{-}{R}$; R being any monovalent anion. Such operations are usually spoken of as "oxidations in the wet way."

Nitric oxide is a colourless gas, very sparingly soluble in water; on bringing it into contact with oxygen, unless moisture is absolutely excluded, union takes place to form nitric peroxide, NO_2, along with a trace of N_2O_3, nitrous anhydride. On sufficiently cooling nitric oxide it condenses to a colourless liquid, and at a still lower temperature it forms a white solid.

Nitrous anhydride, strictly speaking, belongs to the class of acid-forming oxides; its formula is N_2O_3. When nitric oxide and nitric peroxide are brought together, only a minute quantity of N_2O_3 is formed; that is, because on converting it into the gaseous state it decomposes almost completely into these products. On cooling such a mixture, however, a blue liquid condenses, which has the formula N_2O_3. It will be afterwards alluded to.

Nitric peroxide, as usually seen mixed with air at ordinary temperatures, is an orange-coloured gas. When pure it condenses to an orange-red liquid, boiling at 22°; it freezes at $-10°$ to a colourless solid. The liquid has a molecular weight corresponding to the formula N_2O_4, and the gas, at temperatures not much exceeding the boiling-point, consists mainly of the same substance. But as the temperature rises the colour grows darker, until, at 140°, it forms a blackish-red gas, consisting wholly of NO_2. With progressive increase of temperature NO_2 dissociates in its turn into NO and O_2, and at 600° the change is complete. As temperature falls the action is reversed.

Neutral Oxides, Class II.—The next class of oxides comprises those which may be termed neutral, because they can act either as bases or as acids, according as they are treated with an acid or with a base. Their hydroxides may be comprised in the same class. A case of this kind has already been explained on p. 70; it is there shown that aluminium hydroxide, when treated with acids, yields salts of aluminium, while with bases aluminates are formed.

Complexity.—It appears probable that such oxides have molecular formulæ more complex than those usually ascribed to them; for instance, aluminium oxide is certainly more complex than is implied by the usual formula Al_2O_3; it may be Al_4O_6 or Al_6O_9, but there is no means at present of determining the degree of complexity of the molecule. The argument in favour of this view is the very high melting-points and boiling-points of such oxides. It is a well-known fact that as the molecular weight of compounds increases the boiling-point rises. Examples to illustrate this are best drawn from carbon compounds, where "polymerism" is not infrequent; that is, where compounds exist having the same percentage composition but molecular formulæ, of which the higher ones are multiples of the lower one. We are acquainted with a series of compounds of carbon and hydrogen, of which the first member is ethylene, C_2H_4; bodies of the formulæ C_4H_8, C_6H_{12}, C_8H_{16}, $C_{10}H_{20}$, &c., are also known; and the boiling-point increases with the molecular weight. Now, the chlorides of the elements are, as a rule, easily volatile, and have low melting-points; and where it happens that both chloride and oxide have a simple molecular formula, as, for example, carbon tetrachloride, CCl_4, and carbon dioxide, CO_2, the chloride has always a higher boiling-point than the oxide. It would appear to follow, therefore, that if the oxides of the metals had as simple molecular formulæ as the chlorides they would show more volatility than the latter. As this is not the case, the presumption is that the oxides possess more complex formulæ than we are in the habit of ascribing to them. This probability will be dealt with as occasion arises.

Among the oxides and hydroxides which exhibit the power of acting both as acid and basic compounds are **cupric hydroxide**, $Cu(OH)_2$, which dissolves in a concentrated solution of potassium hydroxide with a dark blue colour; **zinc** and **cadmium hydroxides**, which dissolve in excess of alkali; sodium zincate has been separated by addition of alcohol, and is precipitated in white needles of the formula $Na_2ZnO_2.8H_2O$; and **aluminium hydroxide**, which dissolves in alkali, forming an aluminate, $MAlO_2$;

stannous and **plumbous hydroxides,** $Sn(OH)_2$ and $Pb(OH)_2$, dissolve in alkalies, forming compounds no doubt analogous to zincates. Chromous, ferrous, manganous, cobaltous, and nickelous hydroxides are not thus soluble. **Chromic hydroxide,** however, is soluble in soda, probably forming a compound like sodium aluminate; unlike the latter, chromium hydroxide is thrown down on boiling the solution.

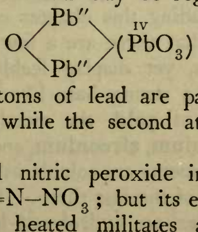
But such compounds, when they do not contain sodium or potassium, are often insoluble in water, and then they cannot be prepared by the action of the one hydroxide on the other. The oxides combine when heated together in the dry condition, and sometimes when the compound formed is decomposed by water (hydrolysed) it is convenient to prepare it either from the oxide or from the carbonate.

Spinels. — A considerable number of compounds, analogous to the aluminates, is produced in this way, and many of them are found in nature as minerals. To this class belong the "spinels," so called because one of their number, the native aluminate of magnesium, had received this name. Viewed as a combination of oxides, such compounds possess the general formula $M_2O_3.MO$, and they can be prepared by heating the sesquioxide (a name given to oxides when the proportion between the metal and the oxygen is as one to one and a half, or, more correctly, as two to three) with the monoxide. The spinels all crystallise in regular octahedra; they are therefore said to be isomorphous with each other. Viewed as aluminates, they may be written $M''(MO_2)_2$; compare $NaAlO_2$. Among them are true **spinel,** $Mg(AlO_2)_2$; **franklinite,** $Zn(FeO_2)_2$; **chrysoberyl,** $Be(AlO_2)_2$; and **chromite,** or "chrome-iron ore," $Fe(CrO_2)_2$. But it is not necessary that the metals of a spinel should be different ones; if a metal is capable of existing in two forms, *e.g.* as dyad and triad, it may form a similar compound. Such are **magnetite,** or "magnetic iron ore," $Fe''(Fe'''O_2)_2$, and

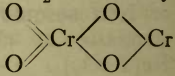
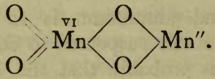
hausmanite, $Mn''(Mn'''O_2)_2$, the first atom of iron or manganese being dyad, like magnesium, and the second triad, like aluminium.

Reasoning by analogy, it would appear not unlikely that native oxides, such as **alumina** (corundum, ruby, sapphire), or **iron sesquioxide** (hæmatite), may be in reality an aluminate of alumina, $Al(AlO_2)_3$, or ferric ferrite, $Fe(FeO_2)_3$.

A common test for zinc and aluminium is to heat together before the blow-pipe the salt suspected to contain the metal with cobalt nitrate; it is probable that the green colour produced by zinc is due to the formation of a cobalt zincate, $Co(ZnO_2)$, and the blue colour shown by alumina to a similar body, $Co(AlO_2)_2$.

When lead is heated to redness in air the first product of its oxidation is litharge, PbO; on continuing the application of heat, at a carefully regulated temperature, the yellow litharge becomes red, and the product of the action is **minium** or "red lead," Pb_3O_4. Now, on treating red lead with dilute nitric acid, lead nitrate dissolves, while lead dioxide, hydrated, remains as an insoluble residue. Red lead, therefore, may be regarded as a compound between two molecules of monoxide and one of dioxide, $2PbO + PbO_2$; the former reacts with nitric acid forming the nitrate, while the latter remains. Now, if the dioxide be heated with caustic potash it dissolves, forming potassium plumbate, K_2PbO_3; and red lead may be regarded as a basic plumbous plumbate,  $O\left\langle\begin{matrix}Pb''\\ Pb''\end{matrix}\right\rangle\overset{\text{IV}}{(PbO_3)}$; "basic," because the first written atoms of lead are partly oxide, partly salt; they are dyad, while the second atom of lead is tetrad.

It is possible to regard nitric peroxide in this light as a nitrate of nitrosyl, $O{=}N{-}NO_3$; but its easy decomposition into NO_2 when heated militates against the view. Compounds of antimony and bismuth, having the formulæ Sb_2O_4 and Bi_2O_4 may be similarly regarded as $O=Sb(SbO_3)$ and $O=Bi(BiO_3)$; of this, however, there is no proof.

Manganese and **chromium** also form "**dioxides,**" to which the simple formulæ MnO_2 and CrO_2 are usually attributed; they, too, may be written  and . They would then be termed chromous chromate and manganous manganate. Such ideas must be regarded as speculative, but there can be little doubt that the formulæ are more complex than they are usually written. The former is a snuff-coloured powder, produced by the action of nitric oxide on a chromate; the latter, formed by oxidising and precipitating a manganous salt simultaneously, is best prepared in a hydrated state by the action of a hypobromite on a manganous salt: $MnCl_2.Aq + NaOBr.Aq + 2NaOH.Aq = O=Mn(OH)_2 + NaBr.Aq + 2NaCl.Aq$. It is a common black mineral in the anhydrous state, and is known as **pyrolusite.** It will be remembered that the ordinary method of preparing chlorine is to heat this mineral with dilute hydrochloric acid, and also that on heating alone it furnishes oxygen, being itself converted into Mn_3O_4, a brown powder, which may be formulated as a spinel, viz. $(O=Mn-O)_2=Mn$.

In concluding this chapter on neutral oxides, it may be mentioned that there are a few which, acting generally as feeble bases, yet display feebly acid properties if in the presence of a strong base like soda or potash. Such are the **oxides** of **gold**, the metals of the **platinum** group, and of **titanium, zirconium,** and **thorium.** The chlorides of these elements are soluble in water, as also the sulphates and nitrates of the last three. Sulphates of gold and platinum, however, are hydrolysed by water, giving oxides and sulphuric acid, thus: $Pt(SO_4)_2 + 2HOH = PtO_2 + 2H_2SO_4$.

Salts of these elements, on treatment with soda, yield no precipitate, for they are dissolved by the alkali; the compounds formed are indefinite, but it may be supposed that they contain aurate, $MAuO_2.Aq$, or platinate, titanate, zirconate, or thorate, $MPtO_3.Aq$, &c. Iron and calcium titanates occur native; $FeTiO_3$ is termed ilmenite, and $CaTiO_3$ perowskite. The first is isomorphous with and crystallises along with native ferric oxide; the ore is known as "titanic iron ore." It is the commonest compound of titanium.

CHAPTER VI

Anhydrides — Acids and Salts — Basic and Acid Chlorides — The Borates — The Carbonates and Thiocarbonates — Other Acids containing Carbon; their Salts with Alcohol Radicals — The Silicic Acids and the Silicates.

Basic Salts.—Many compounds are known which are at the same time chloride and oxide, or chloride and hydroxide of elements. Where the element with which the oxygen and chlorine is combined is one which forms a basic oxide, the compounds in question are termed basic chlorides. Similarly, there are basic bromides and iodides. For example, **zinc** oxide heated with zinc chloride forms **oxychlorides,** of which the simplest example is $Cl-Zn-O-Zn-Cl$; **aluminium** chloride, evaporated with water, has its chlorine gradually replaced by hydroxyl, forming successively $Cl_2=Al(OH)$, $Cl-Al=(OH)_2$, and finally, $Al(OH)_3$, though at a temperature sufficient to complete the reaction, the aluminium would probably form the condensed hydroxide $O=AlOH$ instead of the trihydroxide. We shall see later that other groups, playing a part analogous to that of the chlorine in a basic salt, may also exist in basic salts.

Acid Chlorides.—Another class of double oxides and chlorides exists, most of which are easily volatile, and which therefore are of known molecular weight. These are the so-called "acid chlorides"—oxychlorides of those elements which form acids. These are related to acids, in as much as by replacement of their chlorine by hydroxyl, acids are formed. It will therefore be convenient to consider them along with the acids to which they are related.

A general idea has already been given of the nature of acids in describing the hydroxides of zinc and of aluminium. As a rule, **acids are condensed hydroxides**; that is, hydroxides which, having lost the elements of water, are partly oxides, partly hydroxides. They also possess the property of ionising into one or more hydrogen ions and an electro-negatively charged radical. In following the order of the periodic table, after such feebly acidic hydroxides as those of zinc and aluminium, **hydroxide** of **boron** claims attention.

Borates.—In certain lakes in California the water, when evaporated, deposits crystals of the formula $Na_2B_4O_7.10H_2O$; this substance is named borax. It is a white, crystalline salt, easily soluble in hot water, but sparingly soluble in cold. When mixed with sulphuric acid nacreous scales separate of the formula $B(OH)_3$, or, as it is usual in writing the formulæ of acids to place the hydrogen atoms first, H_3BO_3. **Boracic acid** hardly deserves the name of acid; in aqueous solution it exists almost entirely in the non-ionised state. No ions are volatile; but this compound issues in Tuscany and in the Lipari Islands along with steam from cavities in the ground, termed *suffioni;* it is easily recognised, for it imparts a green colour to a flame held in the steam. When heated to 100° boracic acid loses water and is changed into **metaboracic acid**, O=B–OH, a vitreous substance; and at a red-heat **boron oxide**, B_2O_3, is left as a transparent, colourless glass. Its constitution is O=B–O–B=O.

The **borates** of the **alkalies** are prepared by mixing boracic acid with the hydroxide of the alkali metal; although there are very few hydrogen ions in an aqueous solution of boracic acid, however dilute, yet some of those present combine with the hydroxyl ions of the alkali, forming water, thus: $\overset{+}{H_3}\overset{---}{BO_3}.Aq + 3\overset{+}{Na}\overset{-}{OH}.Aq = \overset{+}{Na_3}\overset{---}{BO_3}.Aq +$

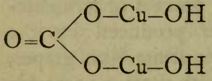
$3H_2O$. But there are so few ions present, that those of the water, which, it will be remembered, is ionised, although to an extremely minute extent, are yet sufficiently numerous to bear some proportion to those of the boracic acid ; hence the reaction given above is perceptibly reversed, and on dissolving borax in water it is "hydrolysed," that is, split by the hydrogen and hydroxyl ions of the water into non-ionised boracic acid and caustic soda, the latter, of course, largely ionised as usual. It is therefore possible to estimate the sodium of borax by addition of a solution of a strong acid, such as hydrochloric or sulphuric acid of known concentration, just as if no boracic acid were present, provided methyl-orange be used as an indicator. (See p. 75.) Thus the addition of 36.5 grams ($H = 1$; $Cl = 35.5$) of hydrochloric acid, dissolved in a litre of water (such a solution is termed a "normal solution"), to 191 grams of a solution of crystallised borax in a litre of water (1/2 [$Na_2 = 46 + B_4 = 44 + O_7 = 112 + 10H_2O = 180$]) ; (in all 1/2 of 382) gives a solution which is neutral to methyl-orange.

Fused borax has the property of dissolving oxides of the metals, forming **complex borates**; certain of these are coloured, and their formation is often made use of for detecting the presence of such metals as copper (blue), silver (yellow), chromium (green), ferric iron (yellow), ferrous iron (bottle-green), manganese (amethyst, when heated in a flame containing excess of oxygen), cobalt (blue), and nickel (reddish). Borax is also used for soldering easily oxidisable metals, such as iron, copper, or brass ; the film of oxide which prevents the metal touching and alloying with the solder is thus removed. Both borax and boracic acid have considerable antiseptic properties, and are used for preserving eggs, milk, and other animal and vegetable substances.

Carbonates and Thiocarbonates. — The **carbonates** and the **thiocarbonates** are derivatives of carbon dioxide (or rather of carbon oxy-hydroxide, commonly called carbonic acid), and of carbon disulphide. Carbon is a tetrad, and the analogue of carbon tetrachloride would be the tetrahydroxide, $C(OH)_4$; but this body is unstable, and its first anhydride, $O{=}C(OH)_2$, is known only in aqueous solution. However, carbonyl chloride, $O{=}CCl_2$, exists; it is produced by the direct union of carbonic oxide with chlorine, when a mixture of both gases is exposed to sunlight; it was formerly known as "phosgene gas," meaning "made by light"; but it is more conveniently prepared by passing a mixture of the two gases over animal charcoal heated to redness. It condenses to a liquid, boiling at 8.4°. It is immediately decomposed by water, thus: $O{=}CCl_2 + 2HOH = O{=}C(OH)_2 + 2HCl$; if sufficient water is present, the carbonic acid can remain in solution. The existence of the oxychloride establishes the formula of carbonic acid.

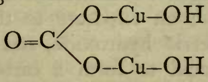
Carbonic acid is a very easily decomposable substance; if liberated, unless a great deal of water be present, it splits into its anhydride, CO_2, and water: $O{=}C(OH)_2 = CO_2 + H_2O$. The anhydride is a colourless gas, which condenses to a solid at about $-80°$; it can be liquefied only under pressure. Carbon dioxide, or carbonic anhydride, is produced by heating a carbonate; as already remarked, all carbonates, except those of the alkaline metals, are decomposed by heat, forming oxides, and evolving carbon dioxide. It is also produced when carbon or carbon monoxide is burned with excess of oxygen. Lastly, it is produced in large quantities during the process of fermentation. Glucose, or grape sugar, either produced by the hydrolysis of starch or extracted from fruits like grapes, when mixed in dilute aqueous solution with yeast, a vegetable organism, decomposes into ethyl alcohol and carbon dioxide, thus: $C_6H_{12}O_6 = 2C_2H_5OH + 2CO_2$. The carbon dioxide being heavier than air, collects in the fermenting tuns; it is now often collected and compressed until it liquefies; and the liquid on expansion solidifies to a snow-like solid, used for producing low temperatures.

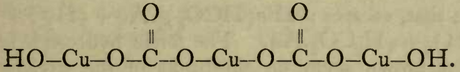
A solution of carbonic anhydride in water contains carbonic acid, $O{=}C(OH)_2$, which is a very weak acid owing to the small extent of its ionisation. It is probable, too, that liquid carbon dioxide exists in the solution, mixed, but not combined with the water. Carbonic acid reacts with **sodium, potassium, calcium**, or **barium** hydroxide, forming **carbonate** of the metal: $\overset{+}{H_2}\overset{--}{CO_3}.Aq + 2\overset{+}{Na}\overset{-}{OH}.Aq = \overset{+}{Na_2}\overset{--}{CO_3}.Aq + 2H_2O$; $\overset{+}{H_2}\overset{--}{CO_3}.Aq + \overset{++}{Ca}\overset{-}{(OH)_2}.Aq = CaCO_3 + 2H_2O$. In such actions it is only the ionised portion of the acid which reacts, and the hydrogen ions form water; when these are removed another portion becomes ionised in order to restore equilibrium; it reacts in its turn until all has become transformed. On evaporation of the solution the alkaline carbonate is left as a white crystalline salt; hydrated sodium carbonate, $Na_2CO_3.10H_2O$, is ordinary washing-soda. All other carbonates are insoluble in water, and are consequently thrown down as precipitates on adding a solution of sodium carbonate to any ionised solution of other metals. They form flocculent precipitates, generally possessing the colour of the ion of the metal; thus **copper carbonate** is blue, **ferrous** green, **cobalt** pink, and so on. But with the exception of the carbonates of the metals of the sodium and calcium groups all other precipitated carbonates are "basic," that is, they are partly hydroxides, partly carbonates. Copper carbonate, for example, may be assigned the formula



; it will be noticed that each atom of copper is combined with the oxygen of the carbonic residue on the one hand, and with hydroxyl on the other. The paint known as "white lead" consists of a basic carbonate of lead, more complex than the example given above, of the formula

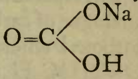
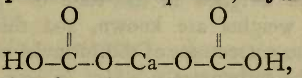
$$HO{-}Pb{-}O{-}(CO){-}O{-}Pb{-}O{-}(CO){-}O{-}Pb{-}OH.$$

Native Carbonates.—Many carbonates exist in the native state; some are widely distributed minerals. Among these are **Iceland** or **calc-spar, arragonite, limestone, chalk**, and **marble**, all of them **calcium carbonate**; **strontianite**, $SrCO_3$; **witherite**, $BaCO_3$; **spathic iron ore**, $FeCO_3$, also named clay-band when contaminated with clay, and black-band when mixed with shale. **Magnesite** is $MgCO_3$; **dolomite**, a mixture of magnesium and calcium carbonates; **calamine**, $ZnCO_3$; and **cerussite**, $PbCO_3$. **Malachite** and **azurite** are basic carbonates of copper, , and



$HO{-}Cu{-}O{-}\overset{\overset{O}{\|}}{C}{-}O{-}Cu{-}O{-}\overset{\overset{O}{\|}}{C}{-}O{-}Cu{-}OH.$

We see here again that with weak bases, such as the hydroxides of most metals, the carbonates tend to become basic, that is, to be hydrolysed. This is why the precipitates obtained on adding a soluble carbonate to a salt of such metals are basic, and not normal carbonates.

"Acid" Carbonates.—The name "**acid carbonate**" is given to a double carbonate of hydrogen and a metal. Such bodies are prepared by the method which always is adopted for the preparation of double salts—by mixture. **Hydrogen sodium carbonate**, ; the corresponding **potassium** compound; **hydrogen calcium carbonate** 

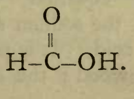
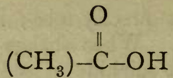
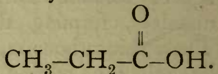
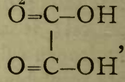
$HO{-}\overset{\overset{O}{\|}}{C}{-}O{-}Ca{-}O{-}\overset{\overset{O}{\|}}{C}{-}OH$, a **ferrous carbonate** of similar formula, and many others are all formed when carbonic acid and the respective normal carbonate are mixed, the mixture being kept cold. On raising the temperature of all of these, carbon dioxide escapes, and the neutral carbonate is again formed. "Acid" carbonate of sodium is the common "baking-soda;" hydrogen calcium carbonate is a constituent of many natural waters, and is the cause of what is termed "temporary hardness"; for on boiling the water the neutral carbonate is precipitated, and the water ceases to be "hard." The same result may be effected, paradoxical as it may appear, by the addition of lime-water; for then sufficient calcium hydroxide is present to form normal calcium carbonate with the hydrogen carbonate, thus: $Ca(HCO_3)_2.Aq + Ca(OH)_2.Aq = 2CaCO_3 + 2H_2O.Aq$. Hydrogen ferrous carbonate is a constituent of chalybeate springs; on exposure to the atmosphere the iron is oxidised to ferric hydroxide, and the carbonic acid, being too weak an acid to form a carbonate with such a weak base as that, escapes: $2Fe(HCO_3)_2.Aq + 5H_2O + O = 2Fe(OH)_3 + 4H_2CO_3.Aq$. The ferric hydroxide is deposited as a brown scum on the banks of the streams flowing from such wells.

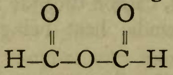
Carbonates of Radicals.—Although normal hydroxide of carbon is unknown, yet if the hydrogen be replaced by ethyl, $-C_2H_5$, the compound is stable. The compound, which is produced by the action of carbon tetrachloride on sodium ethoxide, $CCl_4 + 4Na{-}O{-}C_2H_5 = 4NaCl + C(O{-}C_2H_5)_4$, is the analogue of $C(OH)_4$. It is a volatile liquid, and is named **ethyl orthocarbonate.** And a corresponding **carbonate of ethyl,** $O{=}C(OC_2H_5)_2$, the analogue of carbonic acid, $O{=}C(OH)_2$, is formed by treating carbonyl chloride with alcohol: $O{=}CCl_2 + 2HO{-}C_2H_5 = O{=}C(OC_2H_5)_2 + 2HCl$. These compounds are volatile, and can be weighed in the state of vapour, hence their molecular weights are known, and this is an additional proof of the correctness of the formulæ ascribed to carbonic acid and the carbonates.

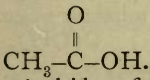
Thiocarbonates.—The sulphocarbonates, or thiocarbonates (from the Greek *theion*, sulphur) form a class of salts analogous to the carbonates, both in their formulæ and in the method of their preparation. Carbon disulphide, a volatile liquid, boiling at 46°, possessing a disagreeable smell, is produced when sulphur vapour is led over charcoal heated to redness in a fireclay tube; in fact, the carbon is burned in sulphur gas. When shaken with a concentrated aqueous solution of the sulphide of sodium or potassium, it dissolves, forming the compound Na_2CS_3, or K_2CS_3. These thiocarbonates, like the carbonates, are white, crystalline salts; on adding acid, **thiocarbonic acid** separates as an oil; it slowly decomposes, especially if warmed, into hydrogen sulphide and carbon disulphide. Many of its salts are insoluble, and may be prepared by precipitation.

The formula of carbon dioxide is CO_2, that of carbon disulphide CS_2; and it is evident that an intermediate substance should exist of the formula COS. This substance is **carbon oxysulphide**. It is a gas, prepared by heating thiocyanic acid, HSCN, the ammonium salt of which is produced when ammonia is passed through a mixture of carbon disulphide and alcohol: $CS_2 + 2NH_3.Alc = H_2S + (NH_4)SCN.Alc$. On evaporation of the alcohol the ammonium thiocyanate crystallises out. This salt, distilled with sulphuric acid, yields in passing the acid HSCN, which, on account of the high temperature, reacts with water, forming ammonia (which yields ammonium sulphate with the sulphuric acid) and carbon oxysulphide, COS: $HSCN + H_2O = NH_3 + COS$.

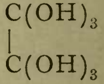
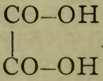
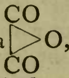
Like nitrous oxide, carbon disulphide is an endothermic compound, and can consequently be decomposed by shock; when a fulminate is exploded in it, it is resolved into carbon and sulphur. On the other hand, carbon dioxide and oxysulphide are exothermic compounds, heat being evolved during their formation.

Acids containing Carbon.—An enormous number of acids containing carbon is known, in which the acidic carbon atom is combined with oxygen and hydroxyl, and also with hydrocarbon residues, such as methyl or ethyl, or with some more complex group of carbon atoms. The simplest of these is formic acid,  $H-\overset{\overset{O}{\|}}{C}-OH$. Acetic acid is methyl-formic acid  $(CH_3)-\overset{\overset{O}{\|}}{C}-OH$; ethyl-formic acid is named propionic acid; its formula is  $CH_3-CH_2-\overset{\overset{O}{\|}}{C}-OH$. Oxalic acid is to be regarded as di-carboxyl,  $\begin{array}{l}O{=}C-OH\\ \quad\ \ |\\ O{=}C-OH\end{array}$, the name carboxyl being a contracted form of "carb(onyl hydr)oxyl"; it is commonly written $-CO-OH$.

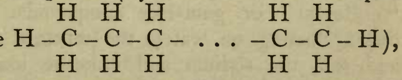
Formic acid (from *formica*, an ant) is contained in ants and stinging nettles. Sodium formate is produced when carbon monoxide is left in contact with sodium hydroxide; the reaction takes a considerable time: $CO + NaOH = H-CO-ONa$. It is also formed by heating oxalic acid, better in presence of glycerine: $(CO-OH)_2 = CO_2 + H-CO-OH$. It is a colourless, pungently smelling liquid, boiling at 99°, and a fairly strong acid in aqueous solution; it is poisonous. Its salts are crystalline, and possess the colours of the metallic ions which they contain. When warmed with concentrated sulphuric acid, or with other substances capable of withdrawing water, it yields carbon monoxide. Yet CO is not the true anhydride of formic acid, seeing that an anhydride can be obtained only from loss of the elements of water from hydroxyl groups, for formic acid contains the group $H-C\equiv$; the real anhydride would be  $H-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-H$; it is unknown.

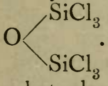
Acetic acid is the acid constituent of vinegar, and is a solid, melting at 17° to a liquid, boiling at 118°. It can be formed synthetically by bringing into contact carbon dioxide and sodium methide, a compound of the formula $Na-CH_3$; the equation is: $Na-CH_3 + CO_2 = H_3C-CO-ONa$; the sodium salt, distilled with sulphuric acid, yields acetic acid. It is produced on a large scale by the distillation of wood; the distillate consists mainly of acetic acid and methyl alcohol; it is neutralised with lime, and distilled, when the alcohol passes over, leaving behind the calcium acetate; this is evaporated to dryness, and heated, so as to char tarry matters, also produced when wood is distilled; the calcium salt is finally distilled with sulphuric acid. Acetic acid is also formed by the oxidation of aldehyde (p. 88), which is itself an oxidation-product of alcohol. The connection between these bodies is: $CH_3{-}CH_2{-}OH$, $CH_3{-}CH{=}O$, and  $CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH$. Aldehyde may be regarded as the anhydride of $CH_3{-}CH{=}(OH)_2$, and acetic acid of $CH_3{=}C(OH)_3$. The usual oxidising agent is chromic acid; if the product of oxidation is conveyed away as it is formed by sloping the condenser downwards, aldehyde is obtained; if the aldehyde is returned to the oxidising mixture by sloping the condenser upwards, and cooling with ice and water, the product is acetic acid. The oxidation is also effected by an organism called "mother of vinegar"; sour wine or beer is allowed to trickle down a cask filled with shavings of beech-wood, on which the slimy masses of the organism are growing; oxygen enters, and the vinegar flows out at the bottom of the cask.

On distilling acetic acid with phosphorus pentachloride, hydroxyl is exchanged for chlorine: $4CH_3{-}CO{-}OH + PCl_5 = 4CH_3{-}CO{-}Cl + H_3PO_4 + HCl$. The compound obtained is named **acetyl chloride**; acetic acid may be regarded as hydroxide of the group $(CH_3{-}C{=}O){-}$, and on treating acetyl chloride with water it is at once formed: $CH_3{-}COCl + H{-}OH = CH_3{-}CO{-}OH + HCl$. And aldehyde may be regarded as a hydride of acetyl, $(CH_3{-}CO){-}H$. A similar body cannot be made from formic acid, for it decomposes into carbon monoxide and hydrogen chloride: $H{-}CO{-}Cl = CO + HCl$.

Oxalic acid is contained as hydrogen-potassium salt in the plants sorrel and rumex. It can be prepared by the oxidation of sugar with concentrated nitric acid, or by heating sawdust with a mixture of caustic soda and potash in shallow trays; on treating the charred residue with water, sodium oxalate, a comparatively insoluble salt, remains, while the excess of alkali dissolves; the sodium oxalate is extracted with boiling water, and calcium chloride is added; this precipitates the almost insoluble calcium oxalate; and on digesting it with the equivalent amount of sulphuric acid, sparingly soluble calcium sulphate remains, while oxalic acid dissolves. The filtered solution, when evaporated, deposits crystals of ortho-oxalic acid,  $\begin{array}{c} C(OH)_3 \\ | \\ C(OH)_3 \end{array}$ which, at 100°, dehydrate to  $\begin{array}{l} CO{-}OH \\ | \\ CO{-}OH \end{array}$. Oxalic acid is a di-basic acid, and its salts, like those of formic and acetic acids, have the colour of the positive ion. It cannot be dehydrated further, for the anhydride, which should possess the formula  $\begin{array}{c} CO \\ \\ CO \end{array}\!\!\triangleright O$, decomposes into CO and CO_2.

Salts of these acids with alcohol radicals, such as methyl and ethyl, are prepared by saturating a solution of the acid in the respective alcohol with hydrogen chloride, and then distilling: $(COOH)_2 + 2CH_3OH = (COOCH_3)_2 + 2HOH$. The hydrogen chloride serves to withdraw water, and prevent it acting on the product. Such salts, which are generally colourless liquids or solids, possessing a pleasant smell, are called "esters." As a rule they are sparingly soluble in water, and are not ionised in solution, thus differing from salts of the metals. When boiled with alkalies, the ester being returned by means of an inverted condenser into the boiling-flask, they change into salts of the alkalies, and the alcohol: $CH_3{-}CO{-}O{-}CH_2{-}CH_3 + KOH.Aq = CH_3{-}CO{-}OK.Aq + CH_3{-}CH_2{-}OH$. This change is also effected by heating with water in a sealed tube; it is accelerated by the presence of hydrogen ions, and therefore by the presence of strong acids, such as hydrochloric acid. Decomposition of this kind by alkalies is called "saponification"; if effected by water the term "hydrolysis" is applied to it.

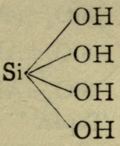
Silicic Acids and Silicates.—While the characteristic of carbon is to form compounds in which many atoms of carbon are linked together (hydrocarbons, for example, having formulæ like  $\mathrm{H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\ldots-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H}$), atoms of silicon are characterised by linking by means of atoms of oxygen. This peculiarity leads to the existence of a large number of **silicates**, and probably, too, of a large number of **silicic acids**. The existence of some of these is rendered certain by a study of the oxychlorides.

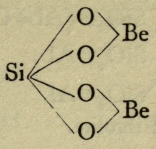
Silicon tetrachloride, $SiCl_4$, when passed over fragments of felspar (a silicate of aluminium and calcium) heated to whiteness in a porcelain tube, exchanges chlorine for oxygen, and yields a liquid boiling at about 137°, of the formula  $O(SiCl_3)_2$. This liquid, passed along with oxygen through a hot glass tube, gave two other liquids, which could be separated by fractionation; the one, boiling at 153°, had the formula $Si_4O_3Cl_{10}$, and the other, boiling at 200°, $Si_4O_4Cl_8$. The vapour-densities of these liquids were determined, and led to the formulæ given above. The signification of this will appear presently.

$Si(OH)_4$. When silica, in the form of flint, or fine sand, or powdered rock-crystal is either fused with caustic soda or potash, or heated under pressure with a solution of one or other of the alkalies, an **orthosilicate** is produced, possessing the formula $Si(ONa)_4$ or $Si(OK)_4$. These silicates are soluble in water, and as they resemble glass in appearance, they are usually named "soluble glass." If hydrochloric acid is added to the solution of one of them, no apparent change occurs; in reality, **orthosilicic acid** is produced, a compound which is hardly ionised at all, being one of the very weakest of acids.

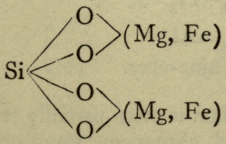
Osmosis.—To separate the ions of sodium chloride and of hydrochloric acid advantage is taken of a discovery made by **Graham**, that a vegetable or animal membrane like parchment or parchmentised paper is readily permeated by crystalline bodies, while it is very slowly permeated by "colloidal" or gum-like compounds. By placing in a drum, floating on water, the mixture of orthosilicic acid and salt, the sodium and chlorine ions pass through, of course in equivalent proportions, leaving the colloid behind. Fresh water is substituted from time to time, until all chlorine ions have been removed from the silicic acid. The water can be removed by evaporation *in vacuo*, and a clear but very viscous liquid remains, which is believed to contain $Si(OH)_4.Aq$. On raising the temperature of this viscous liquid it gelatinises, and is then insoluble in water; the resulting compound may have a formula analogous to carbonic acid, $O{=}Si(OH)_2$; it is termed **metasilicic acid.** On further drying, water is gradually expelled, and finally a flint-like mass is left, which on ignition yields a white powder of SiO_2, or silica. As already mentioned, silica is found in nature; when pure, it crystallises in hexagonal prisms, and is termed quartz, rock-crystal, or Irish diamond. It is used for spectacle lenses and optical instruments.

The major part of the rocks which constitute the surface of the earth consists of mixtures of **silicates.** Occasionally they are found in definite crystals, and on analysis their formulæ can be determined. From their formulæ, the formulæ of the silicic acids from which they may be supposed to be derived can be deduced; and tables follow, in which the formulæ of these silicic acids and of some of the minerals constituting their salts are given.

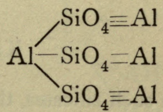




Beryl.

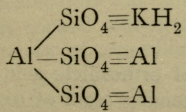


Olivine.

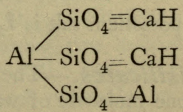


Xenolite.

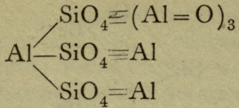
Orthosilicates. — These are orthosilicates; the comma between the Mg and the Fe means that these metals can replace each other in any proportions. Xenolite, it will be observed, is the silicate of a triad metal, aluminium; and four atoms of aluminium replace twelve molecules of hydrogen in three molecules of orthosilicic acid. But double silicates are common, in which three of the atoms of hydrogen in three molecules of orthosilicic acid may be replaced by three monad atoms; or by one dyad and one monad atom; or we may have a monad group, such as $-Al=O$, or $-AlF_2$, replacing each atom of hydrogen; or, lastly, the aluminium may be partly hydroxide, thus constituting a basic silicate. Examples of such compounds are:—

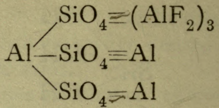


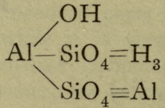
Muscovite, or Potash mica.



Prehnite.

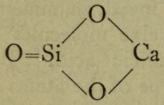

Fibrolite.

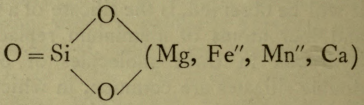

Topaz.

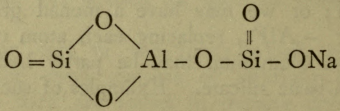

Kaolin or China-clay.

In such silicates, the aluminium is often partially replaced by triad metals, such as triad chromium, iron, or manganese.

Metasilicates.—Metasilicates are derivatives of the acid H_2SiO_3; the constitutional formula is $O{=}Si(OH)_2$, like that of carbonic acid. Examples of metasilicates are:—

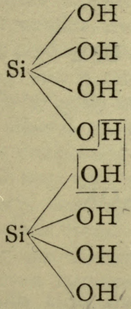

Wollastonite.


Augite or Hornblende.


Jade.

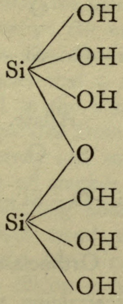
The potassium salt is Leucite.

Disilicates.—The molecules of orthosilicic acid may lose one molecule of water, the remaining atom of oxygen of the two hydroxl groups serving to unite the two molecules together, and a similar loss of water may be repeated twice, thus :—

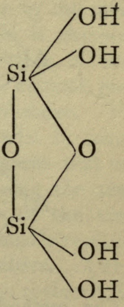


Two molecules of orthosilicic acid.

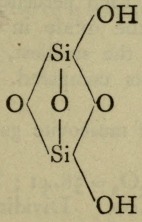
=



Disilicic acid.



1st anhydride.



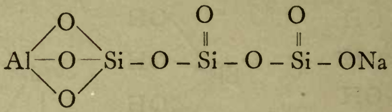
2nd anhydride.

SiO_2

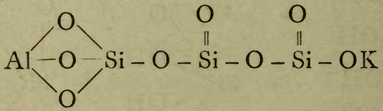
SiO_2

Silica.

The final loss of water yields anhydrous silica. These acids are not known as such ; but certain minerals may be regarded as their salts. It is probable that okenite is a disilicate, thus $CaH_4Si_2O_7$; and also petalite, a derivative of its second anhydride, $AlLi(Si_2O_5)_2$. Similarly, three molecules of orthosilicic acid, by losing two molecules of water, may unite to form trisilicic acid ; and it again by successive loss of one, two, and three molecules of water may yield a first, a second, and a third anhydride. The well-known felspars albite and orthoclase are salts of the third anhydride of trisilicic acid, thus :—



Albite.



Orthoclase.

The method of ascertaining the formula of a silicate requires notice. In order to determine the relative number of molecules of silica, SiO_2, and of the oxides of the various metals in combination with it, each percentage is divided by the molecular weight of the oxide in question; the quotients are then divided by the smallest, and the ratio between the resulting quotients compared. To take an instance :—

An analysis of a specimen of muscovite gave the following numbers :—

$SiO_2 = 45.07$ per cent.; $Al_2O_3 = 38.41$; $K_2O = 12.10$; $H_2O = 4.42$; together = 100.00. Dividing by 60.4; by 102.3; by 94.3; by 18.0, the quotients 0.746, 0.375, 0.128, 0.245 are obtained. Again dividing the quotients by 0.128, the smallest of these quotients, the ratios are: 6, 3, 1, 2, nearly. Therefore the formula is $6SiO_2$, $3Al_2O_3$, K_2O, $2H_2O$, or, adding the various constituents together and dividing by 2, $Si_3O_{12}Al_3KH_2$. The group Si_3O_{12} is $3 \times SiO_4$; the compound is, therefore, an orthosilicate; and three atoms of triad aluminium, one of monad potassium, and two of monad hydrogen are equivalent to the twelve atoms of hydrogen of the three molecules of orthosilicic acid. It sometimes happens, however, that one metal, such as magnesium, may replace more or less of another, such as calcium and iron. In that case, the quotients obtained on dividing the percentages by the molecular weights are added before the final ratio is obtained. The products of Nature's laboratory are seldom, if ever, pure ; and it rarely happens that a natural mineral gives results so easily interpreted as the case given above. For the mineral no doubt separates from a matrix in which many compounds are present; and so it happens that one metal may take the place of another possessing the same valency, and capable of forming compounds of the same crystalline form. The alkali metals are mutually replaceable ; also the triads Al, Fe, Mn, Cr, and others. There are even instances where silicon is partially replaced by titanium ; hence the interpretation of the results of analyses presents a problem of no small difficulty. The work of **F. W. Clarke**, of the U.S. Geological Survey, has contributed not a little to a solution of this problem.

CHAPTER VII

ANHYDRIDES, ACIDS, AND SALTS

Phosphoric, Vanadic, Arsenic, and Antimonic Acids—Nitrous, Phosphorous, Arsenious Acids—Phosphatic Acid—Hyponitrous and Hypophosphorous Acids, and their Salts.

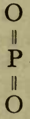
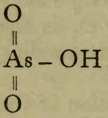
THE remaining hydroxides, which all exhibit well-marked acid functions, may be divided into two classes, those of elements of odd valency, and those derived from elements of even valency. A scheme has already been given on p. 71, which illustrates the derivation of the acids of the halogens from the imaginary hydroxides corresponding to X^{VII}, X^{V}, X^{III}, and X^{I}, where X stands for halogen, and the Roman numerals for the valencies in the compounds.

Elements of Odd Valency.—The highest valency shown by elements of the nitrogen group, apart from a somewhat questionable pernitric acid, is five. This is illustrated by the formulæ of the pentoxides, N_2O_5, P_2O_5, As_2O_5, Sb_2O_5, and V_2O_5. But these compounds possess very different stability, and the elements show different behaviour in uniting with oxygen. Nitrogen and oxygen do not unite except when electric sparks are passed through a mixture of the two gases, or when a high-tension current is passed through air. It is doubtful whether heat alone is the cause of this union; it is more probable that energy must be imparted to the combining gases in an electrical form. The act of combination, in which the product is the peroxide NO_2, is attended by absorption of heat (7700 calories for the union of 14 grams of nitrogen with 32 grams of oxygen) ; and this energy must be supplied if union is to take place. On the other hand, phosphorus burns brilliantly in air, and if excess of oxygen be present, the so-called pentoxide is produced ; according to the vapour-density, however, the formula is P_4O_{10}. If air be slowly passed over heated phosphorus, on the other hand, the lower oxides P_4O_6 and P_2O_4 are formed. It is not possible to dehydrate phosphoric acid, HPO_3, completely, so as to obtain P_2O_5. When arsenic burns in air, arsenious oxide, As_4O_6, is the product ; with antimony, Sb_4O_6 ; but vanadium pentoxide, V_2O_5, is formed when the element or one of the lower oxides is heated in air.

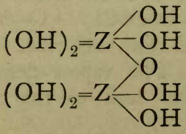
The pentoxides behave differently when treated with water. While N_2O_5 and P_4O_{10} unite with water with a hissing noise to form HNO_3 and HPO_3, As_4O_{10} slowly reacts to produce H_3AsO_4, and probably H_3VO_4 is the result of dissolving V_2O_5 in water ; the corresponding Sb_2O_5 is insoluble in water.

Acid Chlorides.—The clue to the constitution of the acids of these elements is afforded by the oxychlorides, as in the case of carbon and silicon. No oxychloride containing pentad nitrogen is known, but **phosphoryl chloride**, $O{=}PCl_3$, and **antimonyl chloride**, $O{=}SbCl_3$, are produced by the action of a small quantity of water on the respective pentachlorides : $Cl_2{=}PCl_3 + H_2O = O{=}PCl_3 + 2HCl$. The former is a colourless liquid boiling at 107°, and the latter a white, crystalline solid. Phosphoryl chloride reacts with hydrogen sulphide, yielding the corresponding **phosphoryl sulphide**: $O{=}PCl_3 + H_2S = S{=}PCl_3 + H_2O$, and hydrogen sulphide acts on antimony pentachloride, with formation of $S{=}SbCl_3$. $O{=}VCl_3$ is produced by direct union of VO with chlorine. It is a yellow liquid boiling at 137°. The vapour-densities of phosphoryl and vanadyl chlorides lead to the ascribed formulæ.

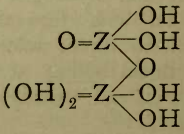
Ortho-, Pyro-, and Meta-Acids.—With water, these substances exchange chlorine for hydroxyl, thus: $O{=}PCl_3 + 3H{-}OH = O{=}P(OH)_3 + 3HCl$. This establishes the formula of **ortho-phosphoric acid.** The name ought, in strictness, to be applied to $P(OH)_5$; but, as the true ortho-phosphoric acid is unknown, it has been transferred to what should be termed its first anhydride. The corresponding nitric acid is unknown. We have thus the series: $O{=}PCl_3$, $O{=}P(OH)_3$, $O{=}As(OH)_3$, and $O{=}Sb(OH)_3$.

On heating these bodies the elements of water are lost, and the "**meta-acids**" are formed; at a temperature of about 200°, $O{=}P(OH)_3$ yields  $\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{P}}-OH$, and $O{=}As(OH)_3$,  $\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{As}}-OH$; the former is a glass, the latter a pearly substance. On adding water to **metaphosphoric acid** it dissolves as such, and, on neutralisation, it yields a series of metaphosphates; but **metarsenic acid,** when treated with water, is reconverted into orthoarsenic acid; a similar change can be produced with metaphosphoric acid, but only after prolonged boiling.

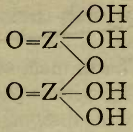
Di-Acids.—We are unacquainted with any normal di-acid of this group, but a number of anhydrides are known. If Z stand for any element of this group, the series should run as follows:—



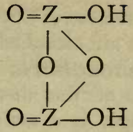
Di-acid.



1st Anhydride.



2nd Andryhide.



3rd Anhydride.

Neither the di-acid nor the first anhydride are known in any case, but the second anhydride, which is generally called the "pyro" acid, because it is formed in certain cases by heating the "ortho" acid, is known with phosphorus, arsenic, antimony, and vanadium. **Pyrophosphoric acid** is formed at 215°; but the change is not complete, and if a higher temperature be employed the meta-acid is also produced. **Pyroarsenic acid** is formed by heating the ortho-acid to 140°–160°. **Pyroantimonic acid,** however, is best prepared by the action of boiling water on antimonyl chloride, $O{=}SbCl_3$; the ortho-acid, which is probably formed first, loses the elements of water, forming the pyro-acid, $H_2Sb_2O_7$. Pyro-phosphoric acid is a syrupy glass-like substance; pyro-arsenic acid forms hard crystals, and pyro-antimonic acid is a sparingly soluble white powder.

Basicity.—The basicity of these acids is deduced from the formulæ of double salts. Thus, there are three orthophosphates of sodium and hydrogen; they have the formulæ H_2NaPO_4, HNa_2PO_4, and Na_3PO_4; the hydrogen calcium salts are: $H_4Ca(PO_4)_2$, $HCaPO_4$, and $Ca_3(PO_4)_2$. It is therefore argued that since the hydrogen atoms of ortho-phosphoric acid are replaceable in three stages by metals, there are therefore three atoms of hydrogen. These salts are made by mixture; $2H_3PO_4.Aq + Na_3PO_4.Aq = 3H_2NaPO_4.Aq$, and so on. The acid is, therefore, said to be tri-basic. The arsenates are precisely similar; but only simple vanadates are known, and no ortho-antimonates. A pyrophosphate is known of the formula $HK_2(NH_4)P_2O_7$, which demonstrates the tetrabasic character of pyrophosphoric acid, and the other pyro-acids are classified accordingly.

Metaphosphoric Acids.—The formula of the third anhydride of the di-acid, $H_2Z_2O_6$, given on the preceding page, is a multiple by two of that of the meta-acid, and it is evident that the fourth anhydride of the tri-acid, the fifth of the tetra-acid, and so on, will all be multiples of the simpler formula of the meta-acid. These acids and some of their salts appear to be known in the case of the phosphoric acids, and what is usually termed "meta-phosphoric acid," and given the formula HPO_3, is probably the seventh anhydride of hexa-phosphoric acid, $H_6P_6O_{18}$, for one of its double salts has the formula $Na_2Ca_5(P_6O_{18})_2$.

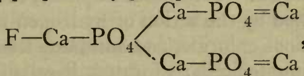
Complex salts are known in the case of almost all these elements. Among such compounds are: $H_2N_4O_{11}$, $Ag_6P_4O_{13}$, $Ag_{12}P_{10}O_{31}$, $Na_6V_6O_{17}$; while niobates and tantalates are particularly prone to form such complex salts. Compounds of a complicated kind, too, in which one of these elements replaces another partially, have been made; as an example, $K_6(P_8V_{12})O_{50}.21H_2O$ may be instanced. They are made by mixture.

The source of the **nitrates** is the attack of ammonium salts resulting from the decomposition of urea (the chief form in which all animals part with the nitrogen they absorb as a constituent of their food) by a bacterium named the "nitrate ferment." This organism exists only in the dark; it is an inhabitant of the soil, and causes the oxidation of ammonia, from whatever source, into a nitrate. As potash and lime are the commonest bases in the soil, nitrates of potassium and calcium are the chief compounds formed. Vast tracts of country in Chili and Peru contain beds of sodium nitrate, possibly formed by the attack of the débris of previous generations of animal organisms by the nitrate ferment. By distilling a mixture of sodium or potassium nitrate with sulphuric acid in glass vessels, or, on a large scale, in iron vessels on which concentrated nitric acid is without action, nitric acid comes over into the receiver: $NaNO_3 + H_2SO_4 = HNO_3 + HNaSO_4$. It is not economical to use the equivalent quantity of sulphuric acid, for the reaction between hydrogen, sodium sulphate, and sodium nitrate takes place at a temperature so high that much of the nitric acid is decomposed: $4HNO_3 = 2H_2O + 4NO_2 + O_2$. **Nitric acid** is a colourless fuming liquid, with very corrosive properties. In aqueous solution it is one of the strongest acids, for it is highly ionised. It is also a powerful oxidising agent; this has been referred to on p. 97. Its **anhydride**, N_2O_5, is produced on distilling a mixture of nitric acid with phosphoric anhydride; the distillate separates into two layers; the upper one consists mainly of N_2O_5, and the anhydride separates in crystals when it is cooled; the lower layer contains $H_2N_4O_{11}$, a liquid solidifying at − 5°; it is the last anhydride of tetranitric acid. The anhydride decomposes spontaneously in a few days into the peroxide, N_2O_4, and oxygen.

Nitrates.—The **nitrates** are all soluble salts, possessing the colours of their metallic ions. As a rule, they crystallise easily. They are all decomposed by heat; those of the metals of the alkalies into nitrite and oxygen; and all others into the oxide of the metal and nitric oxide and peroxide, NO and NO_2. They are formed by dissolving the metal, the oxide, or the carbonate in dilute nitric acid. All metals are attacked by nitric acid, except gold and the metals of the platinum group. The chief nitrates are those of potassium, KNO_3, saltpetre or nitre; of sodium, $NaNO_3$, Chili saltpetre; ammonium nitrate, NH_4NO_3, from which nitrous oxide, N_2O, is obtained on heating; lead nitrate, $Pb(NO_3)_2$, and silver nitrate, $AgNO_3$, still known by its old name "lunar caustic," the word "lunar" referring to the ancient alchemical connection between silver and the moon. It is used as a caustic for removing growths and warts; metallic silver is deposited, blackening the place rubbed.

Phosphates.—The source of **phosphoric acid** and the **phosphates** is chiefly calcium phosphate, $Ca_3(PO_4)_2$, a mineral known as phosphorite, and $AlPO_4$, aluminium phosphate, or gibbsite. Phosphoric acid is produced from phosphorite by heating it with dilute sulphuric acid; sparingly soluble calcium phosphate is formed, while orthophosphoric acid goes into solution. The solution, on evaporation, deposits white crystals of H_3PO_4; the residual liquor deposits crystals of $H_3PO_4.H_2O$; commercial or "glacial phosphoric acid" is a mixture of both kinds. Its solution contains many hydrogen ions, and it is therefore a strong acid. But, inasmuch as phosphoric acid can ionise in three ways, into $3\overset{+}{H}$ and $\overset{---}{PO_4}$, into $2\overset{+}{H}$ and $\overset{--}{HPO_4}$, and into $\overset{+}{H}$ and $\overset{-}{H_2PO_4}$, there are three kinds of anions. The first of these, $\overset{---}{PO_4}$, are present in very small relative amount; the second and-third, $\overset{--}{HPO_4}$ and $\overset{-}{H_2PO_4}$, are relatively much more numerous. There is a state of balance between the quantities of these ions present in any solution; and if, for example, kations of calcium or lead or silver be added to a solution of phosphoric acid, or to one of hydrogen di-sodium phosphate, Na_2HPO_4, the $\overset{---}{PO_4}$ ions present enter into combination with the kations, forming $Ca_3(PO_4)_2$, $Pb_3(PO_4)_2$, or Ag_3PO_4; the $\overset{---}{PO_4}$ ions are increased at the expense of the $\overset{--}{HPO_4}$ and $\overset{-}{H_2PO_4}$ ions, and the solution becomes more acid. On adding an alkali, *e.g.* caustic soda, to a solution of phosphoric acid, neutrality occurs when the salt Na_2HPO_4 has been reached; the ions are then mainly $2\overset{+}{Na}$ and $\overset{--}{HPO_4}$. On adding more soda, the solution becomes alkaline, indicating the presence of free $\overset{-}{OH}$ ions; and it is only on concentration that these $\overset{-}{OH}$ ions combine with the few $\overset{+}{H}$ ions of the ionised, $\overset{+}{\mathrm{Na}}_2\overset{+}{\mathrm{H}}\overset{---}{\mathrm{PO}_4}$, forming non-ionised water, and "tribasic" sodium phosphate, Na_3PO_4, is left as a residue. Similar remarks apply to the **ortho-arsenates.** The **ortho-vanadates** are hydrolysed by water into pyro- and meta-vanadates.

The chief **orthophosphates** are : $Na_2HPO_4.12H_2O$, obtained by neutralising phosphoric acid with sodium carbonate ; $HNa(NH_4)PO_4.4H_2O$, named "microcosmic salt" ; the human organism used to be known as the "microcosm," and this salt crystallises out of concentrated urine ; $Ca_3(PO_4)_2$, prepared by precipitation, and found native as phosphorite ;



$$\mathrm{F{-}Ca{-}PO_4}\left\langle\begin{array}{l}\mathrm{Ca{-}PO_4{=}Ca}\\ \mathrm{Ca{-}PO_4{=}Ca}\end{array}\right.$$

, a widely spread mineral termed apatite ; $(NH_4)MgPO_4.6H_2O$, a white precipitate produced by adding ammonium and magnesium ions to those of a soluble phosphate : $\overset{+}{(\mathrm{NH}_4)} + \overset{++}{\mathrm{Mg}} + \overset{---}{\mathrm{PO}_4} = (\mathrm{NH}_4)\mathrm{MgPO}_4$. It is the usual test for the presence of magnesia, and serves at the same time to distinguish phosphoric acid ; arsenates give a precisely similar precipitate. The precipitate is nearly insoluble in ammoniacal water, and it may be filtered off and washed with water containing ammonia with very little loss. Like almost all phosphates, it is soluble in water containing hydrogen ions ; and by the addition of ammonium hydroxide their number is greatly diminished. On ignition, it yields magnesium pyrophosphate, $Mg_2P_2O_7$, thus : $2Mg(NH_4)PO_4 = Mg_2P_2O_7 + 2NH_3 + H_2O$.

Arsenates.—The important **arsenates** correspond exactly in formula and crystalline form to the phosphates ; the only striking difference is in the colour of the silver salt ; while ortho-phosphate of silver is yellow, the ortho-arsenate is brick-red.

Vanadates.—**Ortho-vanadates** are prepared by fusing vanadium pentoxide with the required amount of a carbonate ;

on addition of nitric acid to one of its salts, **metavanadic acid** separates out as a brown-red powder ; on ignition, a sparingly soluble red powder is left: $2HVO_3 = H_2O + V_2O_5$. Ortho-antimonates are unknown.

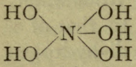
Thio-Acids.—**Thio-compounds** are known, analogous to these salts. Mention may be made of mixed oxy-thio-phosphates, *e.g.* Na_3PO_3S and Na_3POS_3, which result from the action of alkaline hydroxides on phosphorus pentasulphide, a grey solid produced by direct combination of phosphorus with sulphur. They are easily decomposed by hot water; hence the **thio-arsenates** and the **thio-antimonates** are better known. Arsenious sulphide, As_2S_3, a yellow precipitate formed by the action of hydrogen sulphide on a solution of arsenious chloride, and antimony trisulphide, Sb_2S_3, an orange precipitate similarly formed, dissolve in solutions of polysulphides of the alkalies; these solutions, on evaporation, deposit crystals on cooling: $As_2S_3 = 2K_2S^1_n.Aq = 2K_3AsS_4.Aq + S_{(n-2)}$. Sodium thio-antimonate, $Na_3SbS_4.9H_2O$, has long been known as "Schlippe's salt." One of the sulphur atoms may be replaced by selenium, giving $Na_3SbS_3Se.9H_2O$, thus showing the similarity in character between sulphur and selenium.

Pyrophosphoric Acid.—When hydrogen di-sodium orthophosphate is heated to redness, water is lost, and tetra-sodium pyrophosphate is left as a white deliquescent mass: $2HNa_2PO_4 = Na_4P_2O_7 + H_2O$. This salt is soluble in water. On adding to it lead nitrate, a precipitate of lead pyrophosphate is thrown down; it is filtered off, suspended in water, and a current of hydrogen sulphide is passed through the liquid. Lead sulphide is formed, and, on removing it by filtration, the solution contains pyrophosphoric acid. With silver nitrate, a pyrophosphate gives a white precipitate of silver pyrophosphate, a reaction which distinguishes this acid from orthophosphoric acid, for silver orthophosphate is yellow. Magnesium pyrophosphate has already been alluded to. The pyrophosphates of the metals, those of the alkalies excepted, are insoluble in water, but, for reasons similar to those given in describing the ortho phosphates, they dissolve in acids.

Pyroantimonate of potassium is a salt obtained by fusing the metantimonate, $KSbO_3$, with caustic potash, and crystallisation of the resulting fused mass from water. It is easily soluble, but on adding its solution to that of a sodium salt, a precipitate of the sparingly soluble di-hydrogen di-sodium pyroantimoniate, $H_2Na_2Sb_2O_7$, is produced. It is one of the very few sparingly soluble salts of sodium.

Meta-Salts. — On heating to redness di-hydrogen sodium orthophosphate, H_2NaPO_4, or microcosmic salt, $H(NH_4)NaPO_4.4H_2O$, water, or, in the latter case, ammonia in addition, is lost, and the residue consists of **sodium hexa-metaphosphate,** $(NaPO_3)_6$. It is a glass soluble in water; its salts are mostly gelatinous. The acid, which is probably also **hexa-metaphosphoric acid**, is a soluble glass, formed on igniting ortho-phosphoric acid; it yields salts like that mentioned on p. 126. Unlike the other two phosphoric acids, it coagulates a solution of white-of-egg or albumen in water. Its silver salt is white and gelatinous. Mono-metaphosphates are insoluble salts, produced by igniting together oxides, carbonates, sulphates, or nitrates with excess of phosphoric acid, and removing the excess of phosphoric acid with water. The salts of the alkalies are sparingly soluble. **Metarsenates** are produced in a similar manner to the hexa-metaphosphates, but, on treatment with water, they combine with water and re-form the orthoarsenates of metal and hydrogen from which they were obtained. Some pyro- and meta-thioarsenates have been prepared.

Compounds containing less Oxygen. — The elements of the nitrogen group are characterised by their possessing more than one valency. They are also, in most cases, capable of forming compounds with hydrogen. These two characteristics, taken together, lead to the possibility of their forming a number of isomeric compounds, *i.e.* compounds having an identical composition, but being, at the same time, different chemical individuals. Some such compounds are known, at least in their derivatives. The conception will be clearer after inspection of the following table:—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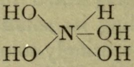
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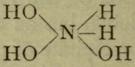
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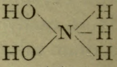
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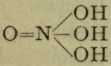
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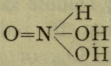
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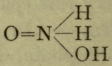
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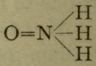
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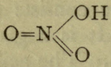
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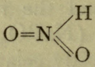
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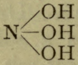
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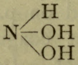
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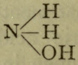
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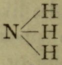
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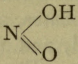
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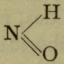
(14)

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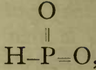
For convenience' sake, the compounds have been written as derivatives of nitrogen, but the type is followed by other elements of the group.

(1) is the true "ortho" acid, unknown in all cases. (9) is its first anhydride, known in "orthophosphoric" acid and in "orthoarsenic" acid. (15) is nitric acid, and corresponds to mono-metaphosphoric acid, metavanadic acid, the metarsenates, and the metantimonates. (2) and (10) are unknown bodies, but (10) corresponds to phosphorous acid, and (16) to the nitrites. (3) is also unknown, but (11) is represented by hypophosphorous acid and the hypophosphites. (4) is unknown. (12), how-

ever, may possibly be the formula of hydroxylamine; its name, in that case, should be "oxy-ammonia." In all these compounds the element is a pentad. The other compounds contain triad element. (5) probably represents the formulæ of the arsenites; (13) is an alternative formula for nitrites. (6) and (14) are unknown. (7) is an alternative formula for hydroxylamine.

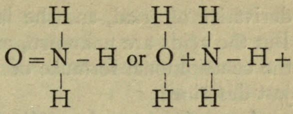
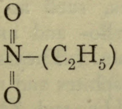
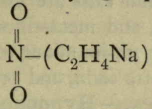
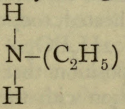
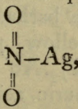
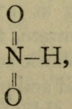
Phosphorous Acid.—We shall first consider numbers (8) and (16). In phosphorous trichloride, PCl_3, phosphorus is undoubtedly a triad. On heating this compound to 60°, and passing over it a current of dry air, and subsequently leading the air through ice-cold water, crystals separate, which are washed with ice-water and dried in a vacuum. They have the formula H_3PO_3. The acid, however, is di-basic; the formula of its sodium salt, for example, is Na_2HPO_3. Again, phosphorous anhydride P_4O_6, produced by the combustion of phosphorus in a limited supply of air, constitutes a crystalline substance, melting at 22.5°; it is acted on only very slowly by cold water, and then yields phosphorous acid. These facts point to a molecular change from $P(OH)_3$ to $O{=}PH(OH)_2$. But this view is rendered certain by consideration of the ethyl salts of the acids.

Constitution of Phosphorous Acid.—Phosphorous trichloride, if treated with a solution of sodium ethoxide, $Na(OC_2H_5)_2$, in alcohol, yields tri-ethyl phosphite, $(C_2H_5)_3PO_3$ or $P(OC_2H_5)_3$, corresponding to $P(OH)_3$. It is a liquid, boiling at 191°. On the other hand, a compound analogous to hydrogen phosphide, PH_3, is known, of the formula $PH_2(C_2H_5)$, named di-ethyl phosphine, which, on oxidation, yields a di-basic acid analogous to phosphorous acid, $O{=}P(C_2H_5)(OH)_2$, named ethyl-phosphinic acid, from which the ethyl salt can be prepared, $O{=}P(C_2H_5)(OC_2H_5)_2$, isomeric with ethyl phosphite. Ethyl phosphite is a derivative of triad phosphorus, whereas di-ethyl ethyl-phosphinate is derived from pentad phosphorus. The anhydride of phosphinic acid,



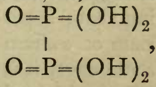
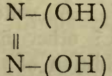
$O{=}PH(OH)_2$, would be, not P_2O_3, but $H{-}\overset{\overset{O}{\|}}{P}{=}O$, like (16). But this substance is not formed on heating phosphorous acid, for it decomposes into phosphoric acid and phosphoretted hydrogen, thus: $4H_3PO_3 = PH_3 + 3H_3PO_4$. One of the varieties of the salts of nitrous acid, however, has a corresponding formula.

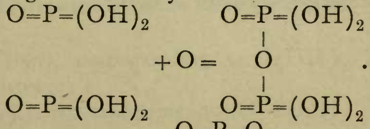
Nitrites.—When a nitrate of one of the metals of the alkalies is heated with metallic lead, lead monoxide is formed, and a nitrite, thus: $KNO_3 + Pb = PbO + KNO_2$. The nitrite is left as a white fusible salt, easily soluble in water. On acidifying a very dilute solution with sulphuric acid, a dilute solution of nitrous acid is formed; but on warming it, a somewhat complex action takes place. First, the anhydride is produced: $2HNO_2.Aq = H_2O.Aq + N_2O_3$; next, the anhydride is attacked by the water and decomposed: $3N_2O_3 + H_2O = 2HNO_3 + 4NO$; and some of the anhydride volatilises with decomposition into nitric oxide and peroxide: $N_2O_3 = NO + NO_2$. The nitrites are white, easily soluble crystalline salts; those of lead, $Pb(NO_2)_2$, and silver, $AgNO_2$, are sparingly soluble. All are decomposed by the stronger acids; for nitrous acid is a weak acid, and, moreover, it is easily decomposed, as has been pointed out. None of these changes throws any light on the constitution of nitrous acid, however. To gain this knowledge it is necessary to study the alkyl salts; for example, ethyl nitrite.

Constitution of the Nitrites. — Ethyl nitrite, made by distilling together a mixture of sodium nitrite, sulphuric acid, and alcohol, is a volatile colourless liquid with a fragrant odour. On boiling it with a solution of sodium hydroxide it is hydrolysed, the ethyl group being again replaced by the metal sodium, thus: $O{=}N{-}O(C_2H_5) + NaOH.Aq = O{=}N{-}ONa.Aq + C_2H_5OH$. And if ethyl nitrite be placed in a flask along with tin and hydrochloric acid—in other words, exposed to the action of nascent hydrogen—the products are ammonia (with some hydroxylamine) and alcohol :  $O = \underset{H}{\overset{H}{N}} - H$ or $\underset{H}{\overset{H}{O}} + \underset{H}{\overset{H}{N}} - H +$ $HO(C_2H_5)$. Sodium nitrite therefore appears to possess the formula $O{=}N{-}ONa$. But silver nitrite, heated in a sealed tube with ethyl iodide, yields a compound of the same composition as, but not identical with, ethyl nitrite, and the formula  $\underset{O}{\overset{O}{N}}{-}(C_2H_5)$ is ascribed to it; for, on heating with caustic soda, it is not hydrolysed, but one of the atoms of hydrogen of the ethyl group is replaced by the element sodium, giving  $\underset{O}{\overset{O}{N}}{-}(C_2H_4Na)$; and further, with nascent hydrogen, the two atoms of oxygen are removed and replaced by hydrogen, yielding ethylamine, a compound analogous to ammonia,  $\underset{H}{\overset{H}{N}}{-}(C_2H_5)$; this shows that the ethyl group in the compound, which is named nitroethane, is in direct union with the nitrogen atom. It appears, then, that silver nitrite has the formula  $\underset{O}{\overset{O}{N}}{-}Ag$, and not $O{=}N{-}OAg$. It also follows that two nitrous acids must exist, $O{=}N{-}OH$ and  $\underset{O}{\overset{O}{N}}{-}H$, the former (13) a derivative of triad, and the latter (16) of pentad nitrogen. But the acids are unknown, and it is only possible to guess the constitutional formulæ of the salts through the reactions just described.

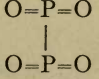
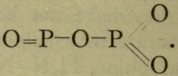
Arsenites. — **Arsenites,** derived from the acid H_3AsO_3, such as hydrogen cupric arsenite or "Scheele's green," $HCuAsO_3$, produced by adding to a solution of copper sulphate potassium arsenite, arsenious oxide, and a little ammonia; pyro-arsenites, such as $K_4As_2O_5$, and metarsenites, $KAsO_2$; also ortho- and meta-thioarsenites, K_3AsS_3 and $KAsS_2$, are known. They show no signs of isomerism like that of the phosphites and nitrites, and they are doubtless salts of $As(OH)_3$ and $O{=}As{-}OH$, and the corresponding sulphur acids, although the acids corresponding to the sulphur salts are unknown. Metantimonite of sodium, $NaSbO_2$, and meta-thioantimonite, $NaSbS_2$, are formed by dissolving antimonious oxide, Sb_4O_6, or the sulphide, Sb_2S_3, in caustic soda, and precipitating with alcohol.

Hypophosphites.—**Hypophosphorous acid,** H_3PO_2, is a monobasic acid; sodium hypophosphite has the formula $Na(H_2PO_2)$. This leads to a formula analogous to that given in (11). When heated, too, the acid yields phosphine and phosphoric acid: $2H_3PO_2 = PH_3 + H_3PO_4$. This would lead to the supposition that some of the hydrogen was already in combination with the phosphorus. Its salts also yield phosphine, together with a phosphate and free hydrogen. The acid is prepared by the action of sulphuric acid on the barium salt; that salt is prepared by boiling together yellow phosphorus and caustic baryta: $2P_4 + 3Ba(OH)_2.Aq + 6H_2O = 2PH_3 + 3Ba(H_2PO_2)_2.Aq$. With sulphuric acid insoluble barium sulphate is formed, while hypophosphorous acid remains in solution. It forms white crystals, melting at 17.4°. The acid has reducing power; with silver nitrate, for example, metallic silver is precipitated and phosphoric acid is formed. With hydrogen iodide phosphorous acid and phosphonium iodide are formed: $3H(H_2PO_2) + HI = 2H_2(HPO_3) + PH_4I$.

Two acids are known belonging to this group of elements; they have not been tabulated on p. 132, because their structure may be compared with that of hydrazine or liquid phosphine, H_2N-NH_2 or H_2P-PH_2, in which two atoms of nitrogen—or of phosphorus—are in direct union with each other. These are **phosphatic acid**, or, as it is sometimes termed, **hypophosphoric acid**,  $\begin{array}{c} O{=}P{=}(OH)_2 \\ | \\ O{=}P{=}(OH)_2 \end{array}$, and **hyponitrous acid**,  $\begin{array}{c} N-(OH) \\ \| \\ N-(OH) \end{array}$. The first of these is produced in small quantity along with ortho-phosphoric and phosphorous acids, when phosphorus is oxidised by exposure to moist air. It is, however, best made from its silver salt, by addition of the equivalent quantity of hydrochloric acid. Silver hypophosphate is produced by dissolving 6 grams of silver in 100 grams of nitric acid diluted with its own weight of water, and adding to the solution, warmed on a waterbath, 8 or 9 grams of phosphorus. As soon as the violent evolution of nitrous gases ceases the liquid is cooled, and silver hypophosphate crystallises out. The acid has no reducing properties, hence it probably contains no hydrogen capable of conversion into hydroxyl by the addition of oxygen. The sodium salt, $Na_4P_2O_6$, is converted into pyrophosphate by the action of a solution of bromine in water; the change is evidently due to the addition of oxygen, thus:



$$\begin{array}{c} O{=}P{=}(OH)_2 \\ \\ O{=}P{=}(OH)_2 \end{array} + O = \begin{array}{c} O{=}P{=}(OH)_2 \\ | \\ O \\ | \\ O{=}P{=}(OH)_2 \end{array}.$$

The anhydride of this acid would be  $\begin{array}{c} O{=}P{=}O \\ | \\ O{=}P{=}O \end{array}$; a compound of the formula P_2O_4 is produced by the incomplete combustion of phosphorus in oxygen; but as it yields orthophosphoric and phosphorous acids on treatment with water, it is in all probability phosphoryl phosphate,  $O{=}P{-}O{-}P\begin{matrix}\diagup O\\ \diagdown O\end{matrix}$.

Hyponitrites are produced by the action of sodium amalgam, that is, a solution of sodium in mercury containing about 4 per cent. of the former, on a solution of potassium or sodium nitrite. After the mixture has stood for some days, it is rendered slightly acid with acetic acid, and silver nitrate is added. A yellow precipitate of silver hyponitrite is produced ; other hyponitrites may be prepared from it by the addition of the calculated quantity of the respective chloride. The acid can also be liberated by the addition to a very dilute aqueous solution of the equivalent amount of hydrochloric acid. On warming the solution of the acid, nitrous oxide is evolved ; but nitrous oxide does not unite with water to form the acid.

That the acid has the formula $H_2N_2O_2$, and not HNO, is shown by its formation from hydroxylamine and nitrous acid. On mixing dilute solutions of hydroxylamine sulphate and sodium nitrate, the hydroxylamine nitrate loses water, thus: $HO{-}NH_2 + O{=}N{-}OH = H_2O + HO{-}N{=}N{-}OH$; the silver salt is thrown down on addition of silver nitrate.

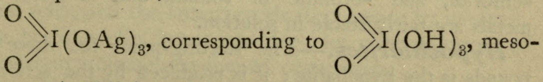
CHAPTER VIII

The Oxy-Acids of the Halogens; Perchlorates and Periodates; Chlorates, Bromates, and Iodates; Chlorites; Hypochlorites, Hypobromites, and Hypoiodites—Acids and Salts of Sulphur, Selenium, and Tellurium; of Molybdenium, Tungsten, and Uranium—Perchromates, Persulphates, Perborates, and Percarbonates.

THE formulæ of the acids of the halogens present some analogy with those of the nitrogen group, for, like the latter, the halogens also possess uneven valency. But while the highest valency of elements of the nitrogen group is that of a pentad, chlorine and iodine function as heptads in perchloric and periodic acids. The valency of the halogens is five in chloric, bromic, and iodic acids; three in chlorous acid; and one in the hypochlorites, hypobromites, and hypoiodites. A short table, analogous to that given on p. 132, shows the relation between these compounds:—

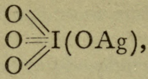
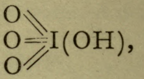
$I(OH)_6(ONa)$, corresponding to $I(OH)_7$, ortho-periodates;

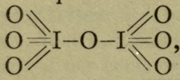
$O{=}I(OAg)_5$, corresponding to $O{=}I(OH)_5$, para-periodates;



$\begin{matrix}O\\O\end{matrix}{>}I(OAg)_3$, corresponding to $\begin{matrix}O\\O\end{matrix}{>}I(OH)_3$, meso-

(middle) periodates;

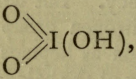
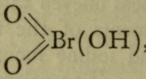
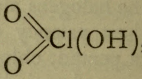
, corresponding to , meta-periodates.

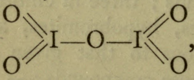
, unknown periodic anhydride.

Perchloric acid, $O_3Cl(OH)$, corresponding to meta-periodic acid, is the only representative of these among the other members of the halogen group. But the periodates, like the phosphates, form still more condensed acids ; thus, salts of a di-ortho-periodic acid, $H_8I_2O_{11}$, and of a di-meso-periodic acid, $H_4I_2O_9$, as well as of a tetra- and hexa-periodic acid, $H_{10}I_4O_{19}$ and $H_{20}I_6O_{21}$, are known.

$I(OH)_5$, ortho iodic acid ; orthobromic and ortho chloric acids are unknown.

$O=I(OH)_3$, and similar bromine and chlorine acids, are unknown.

, , and , iodic, bromic, and chloric acids.

, iodic anhydride, is the only anhydride known.

A tri-iodic acid, HI_3O_8, has been prepared.

$O=Cl-(OH)$, **chlorous acid**, is the only representative of triad halide.

$I-(ONa)$, $Br-(ONa)$, and $Cl-(ONa)$, hypoiodite, -chlorite, and -bromite of sodium and of some other metals are fairly stable in solution.

Hypochlorites.—The starting-point for these compounds is the hypohalite ; it is produced by the action of a hydroxide on the element in cold aqueous solution, thus :

$2NaOH.Aq + Cl_2$, Br_2, or $I_2 = NaCl$, NaBr, or $NaI.Aq + H_2O + NaOCl$, NaOBr, or NaOI.Aq.

Chlorine monoxide, Cl_2O, is formed on passing over dry mercuric oxide, prepared by precipitation from mercuric chloride with caustic soda, dry chlorine gas; the tube containing the oxide must be cooled with ice, for the monoxide is a dark brown, very unstable liquid, boiling at 6°. The equation is: $2HgO + 2Cl_2 = Hg_2Cl_2O + Cl{-}O{-}Cl$. Its density at 10° corresponds with the formula given. If the mercuric oxide be made into an emulsion with water, and chlorine be passed through, the **acid** is produced in aqueous solution; it is a pale yellow liquid, with a not unpleasant smell, recalling that of chlorine. If concentrated, it decomposes into water, chlorine, and oxygen. It reacts at once with hydrochloric acid, forming water and chlorine: $H{-}O{-}Cl.Aq + H{-}Cl.Aq = Cl_2 + H_2O.Aq$.

The most important hypochlorite is a double compound, obtained by the action of chlorine on slaked lime, termed "**chloride of lime**" or "**bleaching-powder.**" It is a white, non-crystalline powder, smelling of hypochlorous acid. Its formula is $Cl{-}Ca{-}O{-}Cl$. That it is a compound, and not a mixture of calcium chloride and hypochlorite, is proved by the fact that bleaching-powder is not deliquescent, whereas calcium chloride is a very deliquescent salt; calcium chloride and hypochlorite are both very soluble salts, but bleaching-powder is only sparingly soluble, but if a saturated solution of bleaching-powder be cooled, crystals of hypochlorite separate out, thus proving that it is dissociated in aqueous solution into these two salts. Its smell, as well as that of other hypochlorites, is due to the fact that hypochlorous acid is a very feeble acid, and is only slightly ionised; hence the calcium and other salts are hydrolysed by the ions of water, and the solution contains free base and free acid; and the latter reveals its presence by its smell. No ion has a smell; hence one does not smell solutions of salts, but only volatile non-ionised compounds.

When bleaching-powder is distilled with just enough acid to liberate the hypochlorous acid, that acid comes over; but if excess of such an acid as sulphuric or hydrochloric be added, chlorine is liberated, owing to the reaction between hydrochloric and hypochlorous acids. The addition of a trace of a salt of cobalt to bleaching-powder results in the liberation of oxygen when it is warmed; this reaction, which is termed "catalytic," is supposed to be due to the alternate formation and decomposition of an oxide of cobalt of the formula Co_4O_7; but the reaction is still obscure. The bleaching action of bleaching-powder in presence of acid is ascribed to the liberation of oxygen, and the oxidation thereby of the insoluble brownish colouring matter of unbleached cotton or linen to soluble compounds which can be removed by washing.

Chlorates. — Hypochlorites, when heated, undergo conversion into a mixture of **chlorate** and **chloride**: $3NaOCl.Aq = NaClO_3.Aq + 2NaCl.Aq$. The usual method of preparing chlorates, however, is to pass a current of chlorine through hot "milk of lime"—that is, calcium hydroxide suspended and partially dissolved in water. Potassium chloride equivalent to one-sixth of the lime is also present. The following reaction occurs: $6Ca(OH)_2.Aq + 2KCl.Aq + 6Cl_2 = 6CaCl_2.Aq + 2KClO_3.Aq + 6H_2O$. On evaporation, the sparingly soluble potassium chlorate deposits in crystals, leaving the very soluble calcium chloride in solution. The potassium chlorate is purified by recrystallisation. It is a white, lustrous salt, crystallising in flat plates. It fuses readily, and, at a somewhat higher temperature than its melting-point, it evolves oxygen. At the same time some of the chlorate is oxidised by the oxygen, and **perchlorate** is formed: $2KClO_3 = 2KCl + 3O_2$, and $KClO_3 + O = KClO_4$.

Perchlorates.—On ceasing to apply heat, therefore, after the salt has become pasty, and treating with water, the potassium chloride is dissolved, leaving the much less soluble perchlorate; the perchlorate may be purified by recrystallisation.

Owing to the fact that very few potassium salts are insoluble in water, it is not convenient to prepare **chloric acid** from the potassium salt; for this purpose it is better to use the barium salt, made from baryta-water and chlorine; a solution of this salt, when mixed with the equivalent amount of dilute sulphuric acid, yields a precipitate of barium sulphate, and chloric acid remains in solution.

Chlorine Peroxide.—The solution, freed from barium by filtration, may be concentrated by distilling away the water at a low temperature in a vacuum; the acid remains as a colourless, syrupy liquid, which decomposes at 100° into perchloric acid, water and **chlorine peroxide,** ClO_2; the last compound is unstable at that temperature, and explodes into chlorine and oxygen. But the peroxide may be prepared by warming, not above 40°, a mixture of potassium chlorate and concentrated sulphuric acid; the chloric acid decomposes as it is formed: $3HClO_3 = HClO_4 + H_2O + 2ClO_2$. It is a dark red liquid, boiling at 10.6° to a reddish-brown gas. Unlike nitric peroxide, it does not form double molecules; Cl_2O_4 is unknown. It resembles that compound, however, in its action on water; while nitric peroxide gives a mixture of nitrous and nitric acids, chlorine peroxide, added to an alkali, forms a **chlorite** and a chlorate: $2ClO_2 + 2KOH.Aq = KClO_2.Aq + KClO_3.Aq$.

The chlorates, like the nitrates, are all readily soluble in water; lead and silver chlorites, like the corresponding nitrites, are sparingly soluble salts; and lead perchlorate is the only salt which does not easily dissolve. As already mentioned, chloric acid is readily decomposed when its aqueous solution is warmed; chlorous acid is still less stable; but **perchloric acid,** which may be prepared by distilling together potassium perchlorate with concentrated sulphuric acid, is relatively stable, seeing that it can be distilled without decomposition. It is an oily liquid, with acid taste; it is apt to explode when brought into contact with any oxidisable matter. The corresponding perbromic acid is unknown.

Hypobromites.—**Hypobromites** are produced, along with bromides, on mixing solutions of alkalies with bromine; the solution turns yellow, and acquires a smell like that of seaweed. On warming, a change analogous to that suffered by hypochlorites occurs; the hypobromite yields bromide and bromate, and the latter can be separated by crystallisation.

Bromates.—The **bromates** are white salts soluble in water; they do not, however, decompose into bromide and perbromate when heated; the perbromate is unstable, and bromide and oxygen are the only products. Bromic acid, too, when warmed changes to water, hydrobromic acid, bromine, and oxygen; as no compound analogous to ClO_2 is produced, bromous acid is unknown.

Hypoiodites. — The formation of **hypoiodites** is analogous to that of hypochlorites; but the salts are known only in solution mixed with iodide. Again, like the hypochlorites, they change on heating; they yield a mixture of iodide and **iodate**; and from barium iodate iodic acid can be prepared. But it is more readily obtained by boiling iodine with nitric acid; for iodine is more easily oxidised than either chlorine or bromine; or chlorine and water may be used as an oxidising agent.

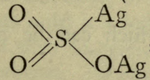
Iodic Acid.—Iodic acid is a white crystalline compound, easily soluble in water; it is a strong acid, and its salts are produced by neutralisation with hydroxides or carbonates. When it is mixed in solution with hydriodic acid, mutual decomposition ensues and iodine is liberated: $HIO_3.Aq + 5HI.Aq = 3I_2 + 3H_2O.Aq$.

Periodic Acid. — The oxidation of iodic acid to **periodic** acid is accomplished by means of a solution of sodium hypochlorite; it is easier to dissolve iodine in a solution of sodium carbonate, when hypoiodite is formed, and to saturate the solution with chlorine. The iodate at first formed is converted into the periodate: $NaIO_3.Aq +$

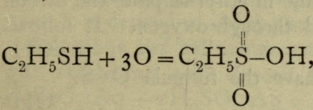
$NaOCl.Aq = NaCl.Aq + NaIO_4.Aq$. As the periodate is sparingly soluble in water, it crystallises out on concentrating the solution. On mixing the solution of the sodium salt with silver nitrate, tri-hydrogen di-argentic periodate is precipitated; it is dissolved in hot dilute nitric acid and evaporated, when mono-argentic periodate, $AgIO_4$, crystallises out. On mixing with water, this salt undergoes the change: $2AgIO_4 + 4H_2O = H_3Ag_2IO_6 + H_5IO_6.Aq$. The silver salt, which is insoluble in water, is removed by filtration, and the **periodic acid** deposits in crystals on evaporation. The acid forms white prisms; on heating it to 130°, it decomposes into **iodine pentoxide**, I_2O_5, a white solid, also produced on heating iodic acid to 170°, together with water and oxygen; at 180° the pentoxide decomposes slowly into iodine and oxygen.

Thermal Data.—From the short description which has been given, it is seen that the oxides of iodine and their compounds are, as a rule, more stable than those of bromine and chlorine, and this is connected with the heat which is evolved or absorbed during their formation. This heat is seldom determined directly; never when the compounds are produced with absorption of heat. Thus, when chlorine combines with oxygen to form Cl_2O, enough heat is absorbed to cool 17,800 grams of water through 1°, or what is the same thing, on decomposing Cl_2O heat enough is liberated to raise the temperature of 17,800 grams of water through 1°. This is termed the heat of formation of the substance. The heat of formation of chloric acid from chlorine, oxygen, and water involves a heat-absorption of 20,400 calories, and these substances are both very unstable. On the other hand, the combination of iodine with oxygen is attended with an evolution of heat of 25,300 calories, and an additional 2600 calories are liberated when it combines with water to form iodic acid. Perchloric acid, too, is formed with evolution of heat (4200 calories), and thus iodic, periodic, and perchloric acid are comparatively stable. The heat-change during the formation of a compound, therefore, is connected with its stability, although the exact relationship between the two is at present unknown.

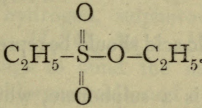
Acids derived from Elements of Even Valency. —**Elements** of the **molybdenum** and of the **sulphur** groups can act as dyads, tetrads, and hexads, and there are corresponding compounds of **chromium**, **manganese**, and **iron**, while sulphur and manganese are also able to form compounds analogous in formula to the perchlorates, termed the **permanganates** and **persulphates**. Compounds in which these elements function as dyads, however, have no acid properties; in the case of chromium, manganese, and iron, the dyad oxides have more or less basic properties—that is, their hydroxides are ionised into element and hydroxyl—and they therefore form salts with acids. The oxides MoO_2 and UO_2 are also feebly basic in character, as well as TeO_2; but MnO_2 is the anhydride of a feeble acid, and SO_2 and SeO_2 form well-defined acids, sulphurous, H_2SO_3, and selenious, H_2SeO_3.

Oxides of Sulphur, Selenium, and Tellurium. The corresponding Acids.—When sulphur, selenium, or tellurium is heated in air, the element takes fire and burns; the chief product in each case is the **dioxide**. That of sulphur is a colourless gas, possessing the well-known odour of burning sulphur; it is condensable to a liquid at -8°, and it freezes at -79°. The gas is soluble in water, uniting with it to form the acid, H_2SO_3; on cooling the solution to -6° and saturating it with the gas, crystals of the formula $H_2SO_3.8H_2O$ separate; this is a hydrate of **sulphurous acid**. Selenious anhydride, a white solid, also dissolves in water, and from the solution **selenious acid** crystallises out, with the formula H_2SeO_3. It would naturally be imagined that these acids should have the structural formulæ $OS=(OH)_2$ and $O=Se(OH)_2$, inasmuch as the oxides are $O=S=O$ and $O=Se=O$; moreover, the chlorides $O=S=Cl_2$ and $O=Se=Cl_2$, thionyl and selenosyl chlorides, are known; and these react at once with water, forming the acids. It is to be presumed that there is exchange of chlorine for hydroxyl, as usual: $O=S=Cl_2 + 2HOH = O=S=(OH)_2 + 2HCl$. But there is evidence, similar in kind to that adduced in the case of nitrous and phosphorous acids, to show that while sodium sulphite has the formula $O=S=(ONa)_2$, silver sulphite is better expressed by  , sulphur being a hexad.

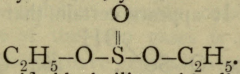
Isomeric Sulphites.—The evidence is this:—Sulphur alcohol or ethyl-hydrosulphide (also termed "mercaptan"), when oxidised by boiling with dilute nitric acid, is converted into ethyl-sulphonic acid, thus:



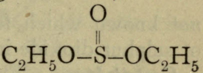
$C_2H_5SH + 3O = C_2H_5\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH$, a monobasic acid, of which the ethyl salt is

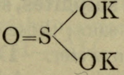


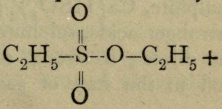
$C_2H_5-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-C_2H_5$. Now sodium sulphite, warmed with ethyl iodide, yields an isomeric compound of the formula



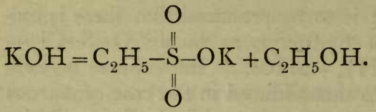
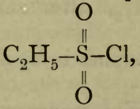
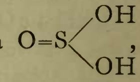
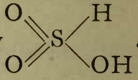
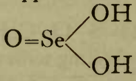
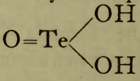
$C_2H_5-O-\overset{\overset{O}{\|}}{S}-O-C_2H_5$. This is known, because when saponified by boiling with alkali, it is converted into alcohol and a sulphite, thus:

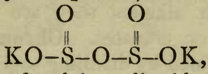


$C_2H_5O-\overset{\overset{O}{\|}}{S}-OC_2H_5 + 2KOH = 2C_2H_5OH + $  ; whereas the saponification of ethyl sulphonate yields potassium ethyl-sulphonate and alcohol, thus:



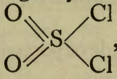
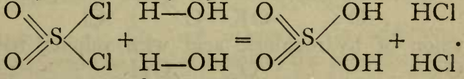
$C_2H_5-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-C_2H_5 +$


$KOH = C_2H_5{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}{-}OK + C_2H_5OH.$ And, moreover, this acid, when distilled with phosphoric chloride, yields an acid chloride,  $C_2H_5{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}{-}Cl$, which can be reduced with nascent hydrogen to ethyl hydrosulphide, the substance from which the acid was originally obtained by oxidation. It is therefore concluded that the carbon is directly united to the sulphur atom in this case, while in ethyl sulphite the carbon of the ethyl group is united through oxygen. It follows that sulphurous acid must have the formula , whereas sulphonic acid should be represented by . The silver salt is a sulphonate, while the potassium salt is a sulphite. This peculiarity is not shown by selenium or tellurium. It appears certain that they are represented by the formulæ  and ; but it is not known which formula is to be ascribed to a solution of sulphur dioxide in water.

Sulphites.—The **sulphites, selenites**, and **tellurites** of the alkalies are soluble salts; those of most of the other metals are sparingly soluble in water. Double salts with hydrogen ("acid salts") are, however, soluble, *e.g.* calcium hydrogen sulphite, $Ca(HSO_3)_2$; and they are all decomposed by the stronger acids, sulphurous acid being liberated, if the solution is dilute; if strong, sulphur dioxide, its anhydride, comes off in the state of gas. Similarly, selenious and tellurous acids are liberated on addition of a strong acid to a solution of a selenite or tellurite. **Pyrosulphites**, similar in kind to pyrophosphates, such as  $KO{-}\overset{\overset{O}{\|}}{S}{-}O{-}\overset{\overset{O}{\|}}{S}{-}OK$, crystallise out on passing a current of sulphur dioxide through a solution of the carbonate of the alkali.

Sulphurous acid is a reducing agent, depriving reducible compounds of their oxygen; it itself is oxidised to sulphuric acid by the process. Owing to this property, it is used to bleach woollen goods; this it does by converting the insoluble colouring matter into a soluble colourless compound, which can be removed by washing. It is also an antiseptic; and sulphites are added to liquors undergoing fermentation, when it is desired to check the action of the ferment.

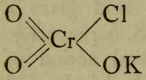
Selenious and **tellurous** acids, treated in boiling solution with sulphurous acid, deposit selenium or tellurium, thus: $H_2SeO_3.Aq + 2H_2SO_3.Aq = Se + 2H_2SO_4.Aq + H_2O$; and with sulphuretted hydrogen, sulphurous acid gives a precipitate of sulphur: $H_2SO_3.Aq + 2H_2S.Aq = 3S + 2H_2O.Aq$. This brings to mind the mutual action of hydrochloric and hypochlorous acids, and of hydriodic and iodic acids, where the elemens are also liberated.

Acid Chlorides. — Sulphur dioxide combines with chlorine when a mixture of the two gases is exposed to sunlight, or when it is passed over gently heated charcoal. The product, **sulphuryl chloride**, , is a colourless fuming liquid, boiling at 77°. On adding it to water, it immediately yields sulphuric acid by replacement of the chlorine by hydroxyl: 

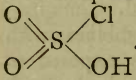
Selenium and **tellurium** form similar compounds; and so also do **molybdenum, tungsten**, and **uranium**, as well as **chromium. Molybdyl, tungstyl**, and **uranyl chlorides**

are produced by passing chlorine over the dioxides heated to redness; they are not decomposed by water, but when boiled with alkalies they are converted into molybdates, tungstates, or uranates. **Chromyl chloride,** on the other hand, is formed by distilling together a chromate, a chloride, and concentrated sulphuric acid. This amounts to the action of hydrogen chloride on chromium trioxide, thus: $CrO_3 + 2HCl = CrO_2Cl_2 + H_2O$. The presence of the sulphuric acid is necessary in order to withdraw and retain water, for chromyl chloride is at once attacked by water, chromic acid being formed. It is a deep red fuming liquid, hardly distinguishable from bromine in appearance; it boils at 118°. A manganyl chloride is said also to have been prepared.

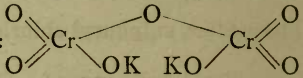
The constitution of the acids is inferred from that of the chlorides; and in the case of chromium, an intermediate body is known between chromyl chloride and potassium chromate, termed **chlorochromate**; its formula is



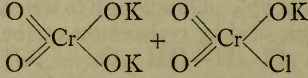
; with sulphur, the corresponding acid, chlorosulphuric, or, better, **chlorosulphonic** acid is known,



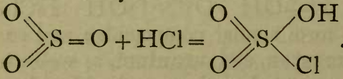
. These bodies are produced by the method of mixture; the former by crystallising together anhydro-chromate and chloride of potassium:



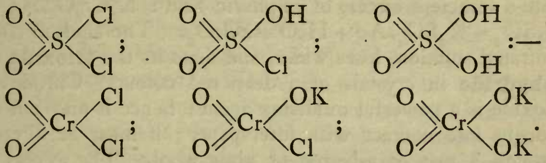
+ KCl =



; the latter, by the union of hydrochloric acid with sulphur trioxide, thus:



. The former consists of red crystals; the latter is a fuming liquid, readily acted on by water, with formation of sulphuric and hydrochloric acids. We have thus with sulphur and with chromium the series :



Chromates.—The starting-point for the **chromates** is chrome iron ore, $Fe(CrO_2)_2$, a spinel (see p. 100). It is heated in a powdered state with a mixture of lime and potassium carbonate, in a reverberatory furnace, where the atmosphere is a strongly oxidising one. The product is a mixture of calcium and potassium chromates and ferric oxide : $2Fe(CrO_2)_2 + 4K_2CO_3 + 7O = Fe_2O_3 + 4K_2CrO_4 + 4CO_2$. The fritted mass is treated with water, when the chromate dissolves, leaving the ferric oxide insoluble. On evaporation, **potassium chromate** crystallises out. If it is desired to produce "**bichromate**" or anhydrochromate of potassium, $K_2Cr_2O_7$, the solution of the chromate is treated with dilute sulphuric acid ; calcium sulphate is precipitated, and is removed by settling ; on evaporation, sparingly soluble sulphate of potassium crystallises out ; and after removal of the crystals, on further evaporation, "bichrome" crystallises. The conversion of the chromate into the anhydrochromate is represented by the equation : $2K_2CrO_4.Aq + H_2SO_4.Aq = K_2Cr_2O_7.Aq + K_2SO_4.Aq$. This conversion is accompanied by a colour-change ; for the ions of chromate, $\overset{--}{CrO_4}$, are yellow, whereas those of anhydrochromate, $\overset{-}{Cr_2}\overset{-}{O_7}$, are orange. On addition of potassium hydroxide to the bichromate, the opposite change takes place ; the anhydro-chromate ion is changed into the chromate ion : $\overset{+}{K_2}\overset{-}{Cr_2}\overset{-}{O_7}.Aq + 2\overset{+}{K}\overset{-}{OH}.Aq = 2\overset{+}{K_2}\overset{--}{CrO_4}.Aq + H_2O$.

Chromic Acid.—**Chromic acid** is liberated on adding to a concentrated solution of potassium anhydrochromate a sufficient excess of sulphuric acid : $K_2Cr_2O_7.Aq + H_2SO_4 = K_2SO_4.Aq + H_2O + 2CrO_3$. The acid, in concentrated solution, loses water, and deposits the **trioxide** or **anhydride** in crystals of a deep red colour. Chromium trioxide is a powerful oxidising agent ; hence it may not be brought into contact with filter-paper ; it must be filtered through a mat of asbestos or glass wool. The excess of sulphuric acid and potassium sulphate are washed out with concentrated nitric acid, in which the anhydride is almost insoluble ; the nitric acid is then volatilised by gentle heat. This anhydride dissolves in water, but it is doubtful whether the acid H_2CrO_4 is contained in the solution ; it is more probable that the ions are $\overset{+\,+}{HH}$ and $\overset{-\,-}{Cr_2O_7}$, from the colour, and other tests, such as the conductivity.

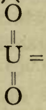
Oxidation by means of a solution of **chromic anhydride** is carried out either by boiling the substance to be oxidised with a mixture of bichrome and dilute sulphuric acid, or with a solution of chromic anhydride in pure acetic acid ; the chromate ion, $\overset{-\,-}{CrO_4}$ or $\overset{-\,-}{Cr_2O_7}$, is changed into the chromic ion $\overset{+++}{Cr}$; the action is : $\overset{+}{K_2}\overset{-\,-}{Cr_2O_7}.Aq + 4\overset{+}{H_2}\overset{-\,-}{SO_4}.Aq = \overset{+++}{Cr_2}(\overset{-\,-}{SO_4})3.Aq + \overset{+}{K_2}\overset{-\,-}{SO_4}.Aq + 4H_2O + \overset{-\,-}{3O}$. If the sulphuric acid is hot and concentrated, oxygen is evolved as gas ; if dilute, substances present in solution, if they are capable of being oxidised, are attacked by the oxygen. When chromic anhydride is heated, it is converted into chromium sesquioxide, Cr_2O_3, with evolution of oxygen.

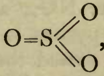
Manganates.—Oxides of manganese, if heated with caustic alkalies in a current of air, or with potassium or sodium nitrate, are converted into **manganate** ; the manganate, however, is much more easily decomposed than the chromate, and, indeed, is stable only in presence of excess of alkali. Manganic acid is incapable of existence ; an attempt to liberate it, by addition of an acid to its sodium salt, results in the formation of a **permanganate** and a manganous salt, thus : $5Na_2MnO_4.Aq + 6H_2SO_4.Aq = 5Na_2SO_4.Aq + MnSO_4.Aq + 4HMnO_4.Aq + 4H_2O$.

Permanganates.—While the manganates are bright green, the permanganates, which are analogous to the perchlorates, are almost black ; they dissolve in water with a deep purple colour ; the best known is the potassium salt, a solution of which is sold under the name of "Condy's Fluid." It is also a useful oxidising agent. If an oxidisable body is boiled with its solution, it loses oxygen, thus : $2KMnO_4.Aq + 3H_2O = 2KOH.Aq + 2MnO(OH)_2 + 3O$; if an acid, such as sulphuric acid, is present, the equation is : $2KMnO_4.Aq + 3H_2SO_4.Aq = K_2SO_4.Aq + 2MnSO_4.Aq + 5O + 3H_2O$.

Ferrates are also known ; they are still more unstable than manganates.

Equations Simplified.—A word may be added here with regard to the somewhat complicated equations such as those given. It is convenient to assume the existence of the anhydride of the acid as a constituent of the salt ; thus potassium bichromate may for this purpose be regarded as consisting of K_2O in union with $2CrO_3$. On acting on it with sulphuric acid in presence of an oxidisable compound, the K_2O may be supposed to react with the acid thus : $K_2O + H_2SO_4 = K_2SO_4 + H_2O$. The chromium salt formed may be regarded (and this was formerly the point of view) as a compound of $3SO_3$, the anhydride of sulphuric acid, with Cr_2O_3, viz., $Cr_2O_3.3SO_3$, or $Cr_2(SO_4)_3$. The formation of Cr_2O_3 from $2CrO_3$ involves the loss of $3O$; hence the equation given above. Similarly, the oxidising action of potassium permanganate may be formulated thus : $K_2O.Mn_2O_7 = K_2O + 2MnO_2 + 3O$; and $K_2O.Mn_2O_7 = K_2O + 2MnO + 5O$. With water present in the former action, the K_2O becomes KOH, and the manganese dioxide becomes hydrated ; with sulphuric acid present in the latter, the K_2O is converted into K_2SO_4, and the MnO into $MnSO_4$. This old method of representing chemical changes had much to recommend it on the score of simplicity; and it often is found convenient, although it is only a partial expression of the truth.

Molybdates, Tungstates, and Uranates.—The formulæ of the **molybdates**, **tungstates**, and **uranates** are analogous to those of the chromates; for example, K_2MoO_4, Na_2WO_4, $(NH_4)_2UO_4$. The common ore of molybdenum is the disulphide, crystalline scales resembling graphite, MoS_2, termed molybdenite. On heating it in the air, or on boiling it with concentrated nitric acid, it is oxidised to the **trioxide**, MoO_3, a white slippery powder. Wolfram, $(Fe,Mn)WO_4$, is the chief ore of tungsten; on boiling with concentrated nitro-hydrochloric acid, calcium nitrate and chloride go into solution, and **tungstic acid**, H_2WO_4, remains as an insoluble yellow powder. On heating it, it loses water, and yields the anhydride, a powder with similar colour, WO_3. Pitchblende is the name of the commonest ore of uranium; its formula is U_3O_8. On fusing it with a mixture of nitrate and carbonate of soda, sodium uranate Na_2UO_4 is formed; and on adding acid, **uranic acid**, H_2UO_4 is precipitated, as a yellow powder. On heating it to 300°, a scarlet powder, of the formula UO_3, remains. Ignition changes it into U_3O_8, possibly uranium uranate, $U(UO_4)_2$, of the same formula as the natural mineral. The chief **molybdate** is that of **ammonium**, $(NH_4)_2MoO_4$, white crystals obtained by dissolving the acid in ammonia solution; it is used in precipitating phosphoric acid as phospho-molybdate of ammonium, a representative of many very complicated molybdates; its formula is $16MoO_3.P_2O_5.3(NH_4)_2O.14H_2O$; it is a derivative of one of the condensed molybdic acids. **Sodium tungstate**, $Na2WO_4$, produced by fusing the trioxide with sodium carbonate, is used as a mordant in dyeing, and it has the property of rendering cotton and linen fabrics uninflammable. The chief characteristic of uranium trioxide is that of forming uranyl salts, such as uranyl nitrate, $(UO_2)(NO_3)_2$, and acetate, $(UO_2)(C_2H_3O_2)_2$, where uranyl,  $\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{U}}=$ acts as a dyad radical. The uranates are ill-defined compounds.

Sulphur Trioxide.—The constitution of sulphuryl chloride and its conversion into sulphuric acid has already been alluded to. And it may be assumed that that of sulphur trioxide, SO_3, is expressed by the formula , sulphur acting as a hexad. Although sulphur dioxide unites directly with chlorine, it does not combine with oxygen, unless the two gases are brought intimately into contact by passing them over finely divided platinum ; such platinum is best prepared by dipping asbestos (a native magnesium silicate, possessing a fibrous structure) into platinic chloride, and subsequent ignition, when the chloride is decomposed into chlorine, which escapes, and a deposit of spongy platinum on the asbestos. On a large scale, sulphur dioxide, made by burning sulphur or iron pyrites, FeS_2, in air, is concentrated by solution in water, the gas being forced in under some pressure ; the solution, on being exposed to reduced pressure, gives up the gas, which is thus freed from the nitrogen of the atmosphere. The sulphur dioxide is then mixed with air and passed over the platinised asbestos heated to a definite high temperature. Combination ensues, and the sulphur trioxide is condensed in cooled receivers. It is a white, crystalline, fuming substance, dissolving in water with a hissing noise and with great evolution of heat. It also unites directly with hydrogen chloride, with formation of chloro-sulphonic acid, $Cl{-}SO_2{-}OH$, a fuming very corrosive liquid.

Sulphuric Acid.—The product on dissolving sulphur trioxide in water is sulphuric acid, H_2SO_4; if smaller quantities of water be used than are necessary for the formation of H_2SO_4, various pyro- or anhydro-sulphuric acids are produced, the simplest of which is the acid, $HO{-}(SO_2){-}O{-}(SO_2)OH$, analogous to some extent in formula to pyrophosphoric acid, $(OH)_2{=}PO{-}O{-}PO{=}(OH)_2$, but more closely resembling potassium dichromate. It, too, is a fuming liquid, evolving much heat on addition of water.

Sulphuric acid, however, is ordinarily made by bringing together sulphur dioxide in presence of steam with nitric peroxide, NO_2, and oxygen. For this purpose, sulphur or iron pyrites is burned in air; the products of combustion are passed through a flue provided with a chamber in which it is possible to place, when required, a pot containing a mixture of sodium nitrate and sulphuric acid; the product is nitric acid, which is at once attacked by the sulphur dioxide, yielding sulphuric acid and nitric peroxide, thus: $2HNO_3 + SO_2 = H_2SO_4 + 2NO_2$. The gases next pass up a tower, termed the "**Glover** tower," after its inventor. In this tower they meet a spray of dilute sulphuric acid, the decomposition product with water of a compound which will afterwards be alluded to, hydrogen nitrosyl sulphate. The hot gases, in contact with the dilute acid, evaporate much of its water, which as steam finds its way along with them up the tower. From the Glover tower the gases enter the first of a series of leaden chambers, in which a reaction occurs between the sulphur dioxide, the nitric peroxide, and the steam, thus: $SO_2 + NO_2 + H_2O = H_2SO_4 + NO$. Excess of air is admitted along with the sulphur dioxide, so that there is present in the leaden chamber a considerable excess of oxygen. By its aid, the nitric oxide is re-oxidised to peroxide, which is again attacked by the sulphur dioxide, so that the nitric oxide serves as a carrier of oxygen to the sulphur dioxide. The nitrogen of the air conveys the gases from chamber to chamber; and when it has passed through a sufficient series (from nine to thirteen) of chambers, all the sulphur dioxide has been converted into sulphuric acid, and deposited on the floors of the chambers, whence it is run off from time to time; it is called "chamber-acid." Formerly, the nitric oxide and peroxide used to escape into the air and be lost, besides causing a nuisance; to save it, **Gay-Lussac** devised a means of trapping it by passing the escaping gases up a tower which bears his name; a stream of concentrated sulphuric acid flows down this tower, moistening the coke or flint with which it is filled. On coming into contact with the mixture of nitric oxide and peroxide, a salt of sulphuric acid is formed—hydrogen nitrosyl sulphate, $HO{-}SO_2{-}O{-}N{=}O$, the group $-N{=}O$ having replaced one of the hydrogen atoms of the sulphuric acid. This compound dissolves in the excess of sulphuric acid; it is conveyed by means of a special pump to the Glover tower, where it is mixed with water, and is decomposed, thus: $2HO{-}SO_2{-}O{-}NO + H_2O = 2HO{-}SO_2{-}OH = NO + NO_2$. Although this compound is formed by the action of concentrated sulphuric acid on a mixture of NO and NO_2, yet excess of water causes the action to proceed in the opposite sense; this affords a good example of the action of mass.

After the chamber acid has been evaporated in leaden vessels until a portion of the water is expelled, it is further concentrated in vessels of platinum, glass, or iron. The dilute acid is without action on lead, and the concentrated acid does not attack platinum or iron, although iron is at once dissolved by dilute acid. The heavy oily liquid remaining after evaporation still goes by its old name of "oil of vitrol." Its composition is not quite expressed by the formula H_2SO_4, however, for that substance is unstable, and parts with a trace of sulphuric anhydride when heated, leaving a trace of water in the oil of vitrol. It can be made by dissolving the right amount of anhydride in the acid to combine with that water; the resulting acid melts at 10.5°; oil of vitrol has a much lower melting-point. The molecular weight of liquid sulphuric acid, determined by its rise in a capillary tube, is very high, and appears to correspond to about $30H_2SO_4$; on dilution it is no doubt considerably lowered, and in dilute solution it is mostly in the state of ions.

When heated to about 250°, sulphuric acid, as oil of vitrol is usually termed, begins to emit fumes of anhydride; apparent ebullition takes place at about 350°, and the acid distils over. This is, however, really dissociation into anhydride and water; for the density of the vapour is not, as might be expected, half the molecular weight, 98, but only 24.5, one quarter of that number. And this agrees with the theoretical density of a mixture in equal proportions of the vapours of the anhydride and water, for $(40 + 9) / 2 = 24.5$. A considerable rise of temperature takes place on mixing sulphuric acid with water; it is not improbable that the first anhydride of the true ortho-acid is formed; the compound of the formula $H_2SO_4.H_2O$, which may be $O{=}S{\equiv}(OH)_4$, melts at 8°. The point of maximum contraction of a mixture of sulphuric acid and water occurs when the proportion corresponds to $H_2SO_4.{}_2H_2O$; this is possibly $S(OH)_6$, but it does not easily solidify. Water can be withdrawn from sulphuric acid by distilling it with phosphorus pentoxide, when sulphuric anhydride is formed and distils over.

Oxidising Action of Sulphuric Acid.—Sulphuric acid can behave as an oxidising agent, being itself reduced. This change is produced when it is heated with most other elements. Thus with carbon, $C + 2H_2SO_4 = CO_2 + 2SO_2 + H_2O$; with sulphur, $S + H_2SO_4 = 3SO_2 + H_2O$; with copper, mercury, iron, lead, silver, &c., a sulphate is formed, and sulphur dioxide is liberated; this may be viewed as the reducing action of hydrogen, at the high temperature required for the reaction, thus: $Cu + H_2SO_4 = CuSO4 + 2H$ and $H_2SO_4 + 2H = 2H_2O + SO_2$. The reduction goes further, and some sulphur is liberated, while copper sulphide is formed: $CuSO_4 + 8H = CuS + 4H_2O$; $H_2SO_4 + 6H = S + 4H_2O$.

Hydriodic, and to a less extent hydrobromic acid also, are oxidised by sulphuric acid: $H_2SO_4 + 2HI = I_2 + 2H_2O + SO_2$; and alcohol and many other compounds of carbon have a reducing action on sulphuric acid.

Selenic Acid.—**Selenic Acid,** H_2SeO_4, is also a colourless syrupy liquid; it can be produced by direct oxidation of selenium by chlorine water, but on concentration the resulting hydrochloric acid reduces the selenic acid to selenious acid, as hydriodic acid reduces sulphuric acid. It is best prepared by addition of copper carbonate to the mixture of selenic and hydrochloric acids obtained in that way; selenate and chloride of copper are formed; the mixture is evaporated to dryness, and the copper chloride is dissolved out with alcohol, leaving the insoluble selenate behind. The selenate is dissolved in water, and on treatment with sulphuretted hydrogen, copper sulphide is precipitated, and removed by filtration; the selenic acid is then concentrated; if it contains a trace of water, it is a heavy liquid; but if quite anhydrous, it forms a solid, melting at 58°.

Telluric Acid.—**Telluric acid** is prepared from its barium salt suspended in water, with the requisite amount of sulphuric acid; the barium salt is produced by heating tellurium with barium nitrate. On evaporation, the hydrate, $H_2TeO_4.2H_2O$, deposits in white crystals.

Sulphate, Selenates, and Tellurates.—The **sulphates, selenates,** and **tellurates** of **barium** are nearly insoluble in water; those of strontium and lead are very sparingly soluble, and those of calcium are still sparingly soluble, though more easily soluble than the salts previously mentioned. All these salts, therefore, are most conveniently prepared by the addition of a soluble sulphate, selenate, or tellurate to a soluble salt of calcium, strontium, barium, or lead, thus: $CaCl_2.Aq + Na_2SO_4.Aq = CaSO_4.2H_2O + 2NaCl.Aq$; $Pb(NO_3)_2.Aq + K_2SO_4Aq = PbSO_4 + 2KNO_3.Aq$. These salts are still less soluble in alcohol than in water, hence addition of alcohol to their solutions produces a turbidity. While barium sulphate is not attacked by boiling hydrochloric acid, barium selenate evolves chlorine, and is changed to barium chloride and selenious acid, thus: $BaSeO_4 + 4HCl.Aq = BaCl_2.Aq + H_2SeO_3.Aq + Cl_2 + H_2O$.

All other sulphates are soluble in water, and can therefore be prepared by one of the usual methods, such as treatment of the oxide, carbonate, or metal with the acid. Dilute sulphuric acid dissolves **magnesium, zinc, cadmium, aluminium, chromium, iron, manganese, nickel**, and **cobalt**; other metals resist its attack, because their electro-affinity is less than that of hydrogen. The order is: Cs, Rb, K, Na, Li, Ba, Sr, Ca, Mg, Al, Mn, Zn, Cd, Cr, Fe, Co, Ni, Pb:—H: Cu, Hg, Ag, Pt &c., Au. All the metals to the left of hydrogen in the table are attacked, because they receive their ionic charge from the hydrogen of the dilute acid: $Zn + \overset{+\ \ --}{H_2SO_4}.Aq = \overset{++--}{ZnSO_4}.Aq + H_2$; the zinc is ionised, receiving its charge from the hydrogen, which escapes in the molecular condition. But this transference of charge appears to require the contact of some metal with lower electro-affinity than that of hydrogen, for pure zinc is not attacked by pure dilute acid; in fact, the arrangement must be analogous to that of a battery. It is possible that this is due to the protection of the zinc by a film of condensed hydrogen—in other words, to polarisation; contact with another metal affords a means of escape of the charge from the hydrogen, which is evolved, not from the surface of the zinc, but from the surface of the less electro-positive metal.

With concentrated acid, these metals, as before remarked, are dissolved as sulphates, with evolution of sulphur dioxide.

The sulphates form an important group of salts. Among the best known are: **Sodium sulphate**, $Na_2SO_4.10H_2O$, "Glauber's salt," contained in sea-water and in many mineral springs; K_2SO_4, and $(NH_4)_2SO_4$, hard rhombic prisms; the double salts, $NaHSO_4$, and $KHSO_4$, obtained by mixture; when heated, these salts lose water and are converted into pyrosulphates: $2KHSO_4 = H_2O + K_2S_2O_7$. $CaSO_4$ occurs native, as **anhydrite**, and $CaSO_4.2H_2O$, as **gypsum** and **alabaster.** Gypsum, when gently heated, loses its water, and is then known as "plaster of Paris;" on mixing it to a paste with water, combination takes place slowly, and the plaster "sets;" and in this way casts may be taken. $SrSO_4$ is found native as **celestine**; $BaSO_4$, as **heavy-spar** or **barytes.** It is the commonest mineral containing barium; from it barium salts are prepared, by heating it with ground coke, which reduces it to the sulphide: $BaSO_4 + 4C = 4CO + BaS$. The barium sulphide is then dissolved in the appropriate acid, and the required salt is made. Precipitated barium sulphate is known as "permanent white;" owing to its low price, it is much used as a paint, although its covering power is small.

$MgSO_4.7H_2O$, $ZnSO_4.7H_2O$, and $CdSO_4.7H_2O$, as well as $FeSO_4.7H_2O$, $MnSO_4.7H_2O$, and the corresponding cobalt and nickel salts, are "isomorphous," that is, they crystallise in the same form—rhombic prisms. **Magnesium sulphate,** or "Epsom salts," is present in sea-water and in many mineral waters; it also occurs in the salt deposits at Stassfurth, in S. Germany, and is termed **kieserite.** It is used as a purgative. **Zinc sulphate** is known as "white vitriol," and **ferrous sulphate** as "green vitriol" or "copperas." A large number of double salts exists, of the formulæ of which $MgSO_4.K_2SO_4.6H_2O$ may serve as a type; they are all soluble, and they are ionised in solution into the same ions as the simple salts would furnish; thus, the ions of the salt mentioned above are $\overset{++}{Mg}$, $2\overset{+}{K}$, and $2\overset{--}{SO_4}$. They differ in this respect from such salts as K_2SiF_6, of which the ions are $2\overset{+}{K}$ and $\overset{--}{SiF_6}$. The **alums** form a similar series of double salts, in which monad metals, such as sodium, potassium, and ammonium, and triad metals, aluminium, chromium, iron, manganese and others, are combined together as sulphates with water of crystallisation: $K_2SO_4.Al_2(SO_4)_3.24H_2O$, or $KAl(SO_4)_2.12H_2O$. The molecular weight of the compound is unknown; hence, as usual, the simpler formula is preferable. These compounds are named from their analogy with the original "alum," of which the formula is given above; they all crystallise in regular octahedra, and, like all true isomorphous salts, they are able to crystallise together; so that if a crystal of $KAl(SO_4)_2.12H_2O$ is placed, for example, in a solution of $(NH_4)_2Cr(SO_4)_2.12H_2O$, the latter will form a dark-red layer on the surface of the former. "Alum" finds use as a **mordant**; when textile fabrics are boiled in its solution, the fibre becomes incrusted with a layer of aluminium hydroxide, and when subsequently dyed the colouring matter is retained in combination with the alumina and with the fibre, so that it cannot be removed by washing. This phenomenon depends on the fact that aluminium sulphate is partially hydrolysed by water into $Al(OH)_3$ and $3H_2SO_4$; the adhesion of the alumina to the fibre is attributed to "adsorption," a term applied to the adhesion of gases, liquids, or of substances in solution, to the surface of solids. A solution of alum also gives coloured precipitates with many dye-stuffs, which are known as "lakes." Selenic acid also yields alums.

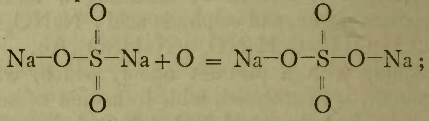
Bismuth sulphate, $Bi_2(SO_4)_3$, obtained by evaporating a solution of bismuth oxide, Bi_2O_3, in sulphuric acid, forms acicular crystals, which, on addition of water, like all other bismuth salts, yield a basic salt, in which the group $O{=}Bi{-}$, bismuthyl, plays the part of a monad metal; hence the formula of the basic sulphate is $(O{=}Bi)_2SO_4$; it is an insoluble powder. **Copper sulphate**, or "blue vitriol," $CuSO_4.5H_2O$, forms blue soluble crystals; **silver, mercurous,** and **mercuric sulphates**, Ag_2SO_4, Hg_2SO_4, and $HgSO_4$, are sparingly soluble, white crystalline powders. As the ion $\overset{--}{SO_4}$ is colourless, all these salts possess the colour of the metallic ion which they contain; thus, $\overset{++}{Fe}$

is green, $\overset{++}{\mathrm{Mn}}$ pink, $\overset{+++}{\mathrm{Cr}}$ green, $\overset{+++}{\mathrm{Fe}}$ yellow, $\overset{++}{\mathrm{Ni}}$ green, $\overset{++}{\mathrm{Co}}$ red, $\overset{++}{\mathrm{Cu}}$ blue, and the others colourless.

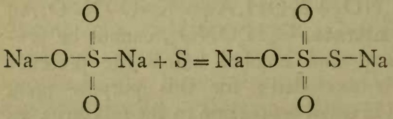
Sulphates of the alkali- and alkaline-earth metals are stable at all temperatures lower than that of the electric arc; but all other sulphates decompose, the primary product being the oxide of the metal and sulphuric anhydride; the latter, however, being unstable at a red-heat, decomposes partly into sulphur dioxide and free oxygen. This decomposition is made use of in the preparation of "**Nordhausen sulphuric acid,**" a fuming liquid, consisting chiefly of $H_2S_2O_7$; it is made by distilling partially dried ferrous sulphate from fireclay retorts: $2FeSO_4 = Fe_2O_3 + SO_2 + SO_3$; the pyrosulphuric acid is produced by the union of the anhydride with water: $2SO_3 + H_2O = H_2S_2O_7$. The iron oxide has a fine red colour, and is sold as a paint under the name "Venetian red."

Salts of Alkyl Radicals.—Salts of the **alkyl radicals** are as a rule volatile; they are produced by distilling the alcohols with the respective acid. **Ethyl nitrite,** for example, is formed by distilling a mixture of alcohol, sodium nitrite, and sulphuric acid: $NaNO_2 + H_2SO_4.Aq + C_2H_5OH = C_2H_5NO_2 + NaHSO_4.Aq$. It is a volatile liquid, with a pleasant odour, which, when boiled with potash, is hydrolysed, with formation of sodium nitrite and ethyl alcohol: $C_2H_5NO_2 + KOH.Aq = K{-}O{-}N{=}O.Aq + C_2H_5OH$. The **nitrate,** $C_2H_5ONO_2$, cannot be prepared from nitric acid and alcohol unless the presence of nitric peroxide is excluded; for this purpose urea, $CO(NH_2)_2$, is added in small proportion to the mixture; its presence prevents the oxidation of the alcohol, and brings about the normal action $C_2H_5OH + HNO_3 = C_2H_5NO_3 + H_2O$. The nitrate resembles the nitrite in properties. On mixing alcohol with sulphuric acid there is a considerable rise in temperature, and **hydrogen ethyl sulphate** is produced: $C_2H_5OH + HO{-}SO_2{-}OH = HO{-}SO_2{-}OC_2H_5 + H_2O$. A considerable excess of sulphuric acid must be present in order to ensure the nearly complete conversion of the alcohol into the ethyl salt. To remove this excess, calcium carbonate is added, which forms sulphate of calcium and a double sulphate of ethyl and calcium, $Ca(C_2H_5SO_4)_2$; the former is nearly insoluble in water, while the latter is readily soluble; from the calcium salt the acid may be produced by addition of the theoretical amount of sulphuric acid. On evaporation it is a syrupy liquid; it decomposes when heated into ethylene, sulphur dioxide, carbon monoxide, and carbon dioxide. As seen by the formula of the calcium salt, the acid is a monobasic one. The potassium salt, for example, has the formula $K(C_2H_5)SO_4$; the salts are all soluble. Similar acids are formed from other alkyl radicals, such as methyl, amyl, &c.

Thiosulphates.—Some other acids of sulphur remain to be noticed. Among these is **thiosulphuric acid**, $H_2S_2O_3$, of which the sodium salt is produced by digesting together sodium sulphite with sulphur, just as, with oxygen, sodium sulphate is formed. In the latter case it may be supposed that the atom of oxygen inserts itself between the sodium atom and the sulphur atom with which it is in combination, thus:



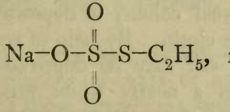
$$\mathrm{Na{-}O{-}}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{\mathrm{S}}}\mathrm{{-}Na} + \mathrm{O} = \mathrm{Na{-}O{-}}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{\mathrm{S}}}\mathrm{{-}O{-}Na};$$

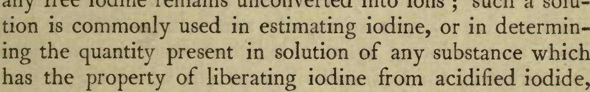


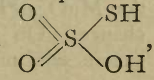
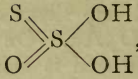
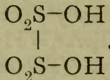
$$\mathrm{Na{-}O{-}}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{\mathrm{S}}}\mathrm{{-}Na} + \mathrm{S} = \mathrm{Na{-}O{-}}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{\mathrm{S}}}\mathrm{{-}S{-}Na};$$

hence the name "thio" sulphate, the "thion," or sulphur, replacing the oxygen of sulphuric acid. The **sodium salt** forms large transparent crystals of the formula $Na_2S_2O_3.5H_2O$; the **barium salt** is sparingly soluble, and forms a crystalline precipitate on adding a solution of the sodium salt to one of barium chloride; the **lead salt** is insoluble, and the **silver salt** is a white precipitate, which rapidly turns dark on application of heat, being converted into silver sulphide: $Ag_2S_2O_3 + H_2O.Aq = Ag_2S + H_2SO_4.Aq$. On acidifying any one of the soluble salts, the acid is momentarily liberated; but it immediately decomposes into sulphurous acid and sulphur, $H_2S_2O_3.Aq = H_2SO_3.Aq + S$, the latter rendering the liquid milky. The sodium salt, when a solution of iodine in one of potassium iodide is added to it, undergoes the reaction: $2Na_2S_2O_3.Aq + I_2.Aq = 2NaI.Aq + Na_2S_4O_6.Aq$. The salt formed is named tetrathionate of sodium. It will be considered shortly.

Iodometry.—A solution of sodium thiosulphate containing 248 grams, made up to a litre with water, reacts quantitatively with one containing 127 grams of iodine per litre; the colour of the iodine disappears, and the vanishing of the last trace of iodine can be ascertained by the addition of some starch paste, which gives a blue colour so long as any free iodine remains unconverted into ions; such a solution is commonly used in estimating iodine, or in determining the quantity present in solution of any substance which has the property of liberating iodine from acidified iodide, *i.e.* from hydriodic acid, such as free chlorine, a hypochlorite, or, indeed, any oxidising agent.

On boiling together solutions of sodium thiosulphate with ethyl iodide, **sodium ethyl thiosulphate** is formed; its formula is  $\mathrm{Na{-}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}{-}S{-}C_2H_5}$, for, when mixed with barium chloride, the barium salt, which is unstable, decomposes into barium dithionate and ethyl disulphide, thus:



This decomposition renders two suppositions probable: that thio-sulphuric acid has the formula , and not , and that dithionic acid is constitutionally represented by 

$$\begin{array}{l} O_2S-OH \\ \quad | \\ O_2S-OH \end{array}$$

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Hydrosulphites.—**Hydrosulphurous acid,** $H_2S_2O_4$, sometimes called "hyposulphurous acid," is produced as zinc salt by the action of metallic zinc on sulphurous acid. The liquid turns brown, and possesses great reducing power. The sodium salt, which is better known, is produced by digesting zinc turnings with a concentrated solution of hydrogen sodium sulphite: $Zn + 4HNaSO_3.Aq = Na_2Zn(SO_3)_2 + Na_2S_2O_4.Aq + 2H_2O$; the sodium zinc sulphite crystallises out on addition of alcohol, leaving the hydrosulphite in solution. On cooling the solution, slender crystals of the hydrosulphite separate. The solution absorbs free oxygen so rapidly that it turns warm; it is used as a reducing agent in indigo-dyeing; indigo-blue is converted by the hydrogen of water (of which the oxygen enters into combination with the hydrosulphite, converting it into sulphite) into a colourless substance, termed indigo-white; this body being soluble, penetrates the fibre of fabrics dipped into the solution, and on exposure to air, indigo-blue, with its usual colour, is deposited as an insoluble precipitate in the cloth. By help of sodium hydrosulphite, too, a ferrous salt may be deprived of ferric so completely that it gives a nearly white precipitate with alkalies; the usual colour of the impure ferrous hydroxide is a dirty green.

Thionates.—Manganese **dithionate** is produced by passing a current of sulphur dioxide through freshly prepared manganese dioxide suspended in water, made by boiling potassium permanganate with alcohol. The equation $MnO_2.nH_2O + 2SO_2.Aq = MnS_2O_6.Aq$ represents the change. On addition of barium hydroxide to the manganese salt, manganous hydroxide is thrown down, and

barium dithionate is left in solution. From it, the **acid** may be prepared by the addition of the requisite amount of sulphuric acid; and the other salts, by addition of the appropriate sulphate. The acid, concentrated by evaporation at a low temperature, is a sour, syrupy liquid; when heated, it decomposes into sulphur dioxide and sulphuric acid.

Trithionic acid, $H_2S_3O_6$, is also known; it is a still more unstable liquid.

Tetrathionate of sodium, as already remarked, is produced by addition of a solution of iodine to a thiosulphate; it is precipitated on addition of alcohol. The acid forms a colourless solution, with strong acid taste. The method of its formation gives a clue to its constitution:

$$\begin{array}{lcccccl} \mathrm{NaO{-}S(O_2){-}S{-}Na} & & \mathrm{I} & & \mathrm{NaI} & & \mathrm{NaO{-}S(O_2){-}S} \\ & + & | & = & + & & \qquad\quad | \;. \\ \mathrm{NaO{-}S(O_2){-}S{-}Na} & & \mathrm{I} & & \mathrm{NaI} & & \mathrm{NaO{-}S(O_2){-}S} \end{array}$$

Pentathionic acid, $H_2S_5O_6$, is produced by passing a current of hydrogen sulphide through a dilute solution of sulphurous acid, along with tri- and tetrathionic acids: $5H_2S + 5SO_2.Aq. = H_2S_5O_6.Aq + 4H_2O + 5S$ is the equation usually given. Excess of hydrogen sulphide, passed for a long time, results in the reaction $2H_2S + SO_2.Aq = 2H_2O.Aq + 3S$. The tri-, tetra-, and pentathionates, when heated, yield a sulphate, sulphur dioxide, and free sulphur.

Highly Oxidised Acids.—Of recent years, a considerable number of salts of acids more highly oxidised than any of those already mentioned has been prepared. It has long been known that on addition of hydrogen dioxide to a solution of potassium bichromate acidified with sulphuric acid, a bright blue colour is produced, and that this coloured substance can be extracted by ether from its aqueous solution. The compound has recently been identified as **perchromic acid,** $CrO_4(OH)$; for, on adding to the cooled blue solution a solution of ammonia in ether, a violet precipitate of $CrO_4(O{-}NH_4).H_2O_2$ is thrown down; and if an etherial solution of potassium hydroxide be added, the potassium salt of similar formula is precipitated. These bodies are explosive.

Persulphates of potassium and ammonium are produced by passing a current of electricity through concentrated solutions of the sulphates in water. The persulphate is sparingly soluble, and deposits in white crystals. The formula appears to be $M_2S_2O_8$ ($M = $ monad metal). The acid has bleaching powers, and gradually decomposes into sulphuric acid and ozone.

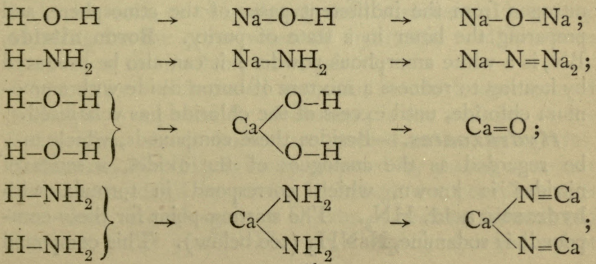
Perborate of sodium, $NaBO_3,4H_2O$, is similarly prepared, or it may be produced by cooling a solution of borax to which some caustic soda and hydrogen peroxide have been added. It, too, is a sparingly soluble salt, possessing bleaching properties.

Percarbonate of sodium, $Na_2CO_4 . 1\frac{1}{2}H_2O$, is similarly prepared by addition of alcohol to a solution of sodium carbonate, to which a solution of hydrogen peroxide has been added. It is a white, extremely unstable compound, possessing, like the other similar salts, great oxidising power.

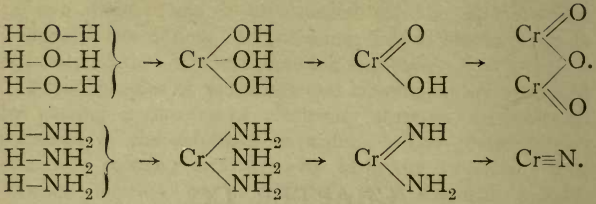
CHAPTER IX

The Nitrides and Phosphides, Arsenides and Antimonides—Complex Amines and their Salts—Acid Amides—The Cyanides and the Double Cyanides.

Analogy between Oxides and Nitrides.—Nitrogen and phosphorus are best characterised by the compounds in which they act as triads. For just as an oxide or hydroxide may, as was customary during the era of the theory of "types," be regarded as water in which the atoms of hydrogen are more or less completely replaced by atoms of a metal; so from analogy it is to be inferred that compounds should be preparable which should be similarly related to ammonia and to hydrogen phosphide. The following graphic formulæ will render the conception clear:—

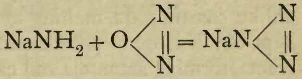


$$\begin{array}{lclcl}
H-O-H & \rightarrow & Na-O-H & \rightarrow & Na-O-Na\,; \\
H-NH_2 & \rightarrow & Na-NH_2 & \rightarrow & Na-N=Na_2\,; \\
\left.\begin{array}{l}H-O-H\\H-O-H\end{array}\right\} & \rightarrow & Ca\left\langle\begin{array}{l}O-H\\O-H\end{array}\right. & \rightarrow & Ca=O\,; \\
\left.\begin{array}{l}H-NH_2\\H-NH_2\end{array}\right\} & \rightarrow & Ca\left\langle\begin{array}{l}NH_2\\NH_2\end{array}\right. & \rightarrow & Ca\left\langle\begin{array}{l}N=Ca\\N=Ca\end{array}\right.\,;
\end{array}$$



But although most elements combine with oxygen directly, there are only a few which burn in nitrogen. Among these are lithium, calcium, and magnesium; boron and titanium also possess this property. The nitrides of the other elements are practically unknown. These nitrides are attacked by water; the three first with violence at the ordinary temperature; the two last, when heated in a current of steam. The products are the hydroxide of the metal and ammonia; or with boron and titanium, owing to the high temperature of action, the oxide, thus: $Mg_3N_2 + 3H_2O.Aq = 3Mg(OH)_2 + 2NH_3.Aq$.

Nitrides.—**Lithium nitride,** Li_3N, is a dark-coloured substance; it is formed at the ordinary temperature on exposing metallic lithium to the air. **Calcium nitride,** Ca_3N_2, is a greyish-yellow substance; and **magnesium nitride,** Mg_3N_2, a yellow powder. Combination takes place readily with great evolution of heat when a mixture of dry lime with magnesium powder is heated to dull redness in a current of nitrogen; this affords a convenient method of separating nitrogen from the indifferent gases of the atmosphere, and preparing the latter in a state of purity. **Boron nitride,** BN, is a white amorphous powder; it can also be produced by heating to redness a mixture of boron oxide with ammonium chloride, until excess of the chloride has volatilised.

Hydrazoates.—Besides these compounds, which may be regarded as the analogues of the oxides, a series of nitrides is known, which correspond in formula with **hydrazoic acid,** HN_3. The starting-point for these compounds is sodamine, $NaNH_2$ (see below). This compound is heated to 300° in a series of small flasks in a current of nitrous oxide, when the following reaction takes place: $2NaNH_2 + N_2O = NaN_3 + NaOH + NH_3$. The change which takes place is more obvious when the reaction is conceived to occur in two stages:  $NaNH_2 + O\left\langle\begin{matrix}N\\ \|\\ N\end{matrix}\right. = NaN\left\langle\begin{matrix}N\\ \|\\ N\end{matrix}\right.$ $+ H_2O$; and $NaNH_2 + H_2O = NaOH + NH_3$. The product of the reaction is dissolved in water, acidified with dilute sulphuric acid, and distilled: $NaN_3.Aq + H_2SO_4.Aq = HN_3.Aq + NaHSO_4.Aq$. The distillate, which is a dilute solution of hydrazoic acid, has a peculiar odour, and if its vapour be inhaled, fainting may result; it is necessary to take precautions to distil it in a good draught. The solution has an acid reaction; salts may be prepared by neutralisation with the hydroxides or carbonates of the metals. The ions, $-N_3$, are colourless, and the salts of colourless ions are themselves white. Those of **lithium, sodium, potassium, magnesium, calcium, strontium, barium,** and **zinc** are crystalline; their formulæ are $M'N_3$ and $M''(N_3)_2$ respectively. **Silver hydrazoate,** AgN_3, closely resembles the chloride in appearance and in insolubility; it is, however, dangerously easy to explode, and should be prepared dry only in minute quantity, and treated with the utmost precaution. Titration with a deci-normal solution of silver nitrate affords a convenient method of determining the strength of a solution of hydrazoic acid, or of analysing the hydrazoates; it is easy to recognise the point when all hydrazoic acid has been removed as the insoluble silver salt.

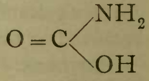
Amines.—Substituted ammonia, in which one atom of hydrogen is replaced by an element, is the analogue of the hydroxides. Such bodies are termed amines or amides. **Sodamine,** $NaNH_2$, is easily prepared by passing a current of ammonia, dried by passing it through a tower filled with soda-lime, through an iron U-tube containing sodium, and heated to about 300°. The gas is rapidly absorbed, while hydrogen is evolved: $2NH_3 + 2Na = 2NaNH_2 + H_2$. When the sodium has been all converted into sodamine, the tube is emptied by pouring out its contents. Sodamine is a white brittle substance, with crystalline fracture, not unlike caustic soda, melting at about 100°. So long as it is kept dry it is quite permanent, but with moisture it at once reacts, forming ammonia and caustic soda: $NaNH_2 + HOH = NaOH + NH_3$. Similar compounds can be made with **lithium, potassium, rubidium,** and probably **cæsium.** The corresponding compound of **zinc,** $Zn(NH_2)_2$, is a white powder, insoluble in ether, formed along with ethane or methane by the action of ammonia on zinc methide or ethide: $Zn(CH_3)_2 + 2NH_3 = Zn(NH_2)_2 + 2CH_4$.

Guanidine.—An attempt to produce the **amine** of **carbon,** $C(NH_2)_4$, by the action of ammonia on such a body as carbon tetrachloride or ethyl orthoformate, $C(OC_2H_5)_4$, according to the equations $CCl_4 + 4NH_3 = C(NH_2)_4 + 4HCl$, or $C(OC_2H_5)_4 + 4NH_3 = C(NH_2)_4 + 4HOC_2H_5$, fails, owing to loss of ammonia. For just as orthocarbonic acid, $C(OH)_4$, loses water, yielding ordinary carbonic acid, so carbon tetramine loses ammonia; the product is named **guanidine,** and has the formula $HN = C(NH_2)_2$; its analogy with $O = C(OH)_2$ is easily seen. Guanidine is a white crystalline substance, which, like ammonia, unites with acids to form salts.

On comparing the formulæ of carbonic acid and guanidine, it is evident that several intermediate compounds should be capable of existence. The series is:—

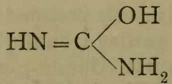
$O = C(OH)_2$ (1)

$HN = C(OH)_2$ (2)


$O = C\begin{cases} NH_2 \\ OH \end{cases}$

(3)

$O = C(NH_2)_2$ (4)


$HN = C\begin{cases} OH \\ NH_2 \end{cases}$

(5)

$HN = C(NH_2)_2$. (6)

Of these, the best known are the ammonium salt of (3), which is termed carbamic acid, and (4), the important compound urea or carbamide.

Carbamates.—**Ammonium carbamate**, known by the familiar name of "smelling salts," is formed by mixing ammonia and carbon dioxide gases: $CO_2 + 2NH_3 = H_2N - CO - ONH_4$. It is a white crystalline compound, soluble in water and smelling of ammonia. Its solution, when fresh, contains the compound of which the formula is given above; but after standing, it is converted by absorption of water into ammonium carbonate. This has been ascertained by treating the freshly prepared solution with sodium hypochlorite, when only half the nitrogen which the substance contains is evolved:

$$2H_2N{-}CO{-}ONH_4.Aq + 3NaOCl.Aq = \\ 2H_2N{-}CO{-}OH.Aq + 3H_2O + 3NaCl + N_2;$$

on the other hand, with a hypobromite, all the nitrogen is evolved:

$$H_2N{-}CO{-}ONH_4.Aq + 3NaOBr.Aq = CO_2 + \\ 3H_2O + N_2 + 3NaBr.Aq.$$

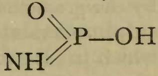
Now, ammonium salts yield up their nitrogen when mixed with a solution of a hypochlorite; hence it is concluded that the compound contained in a fresh solution is ammonium carbamate. But on standing, the solution changes, and after some time it yields all its nitrogen on treatment with hypochlorite; hence the assumption of the elements of water and a change into ammonium carbonate may be inferred: $H_2N{-}CO{-}ONH_4.Aq + H_2O = H_4N{-}O{-}CO{-}ONH_4.Aq$. But ammonium carbamate may conceivably possess the formula $HO{-}C(NH){-}ONH_4$; and it may be that it is the $=NH$ group which resists attack. This last supposition is confirmed by the behaviour of urea with hypochlorite; for with it, too, only half the nitrogen is evolved.

Carbamide.—**Urea** or **carbamide**, to which the formula $O=C(NH_2)_2$ is generally ascribed, is the form in which by far the largest part of the nitrogen is evolved which is consumed as food by animals. It may be directly prepared from urine by evaporation to one-third of its bulk, and addition of nitric or of oxalic acid; the sparingly soluble nitrate or oxalate is precipitated; the salt is purified by recrystallisation from water, and is then mixed with caustic soda and evaporated to dryness. On treatment with alcohol, the urea alone dissolves, and deposits in crystals from a concentrated solution. It is a white, easily soluble substance, with a saline taste. It unites with acids, forming salts; but as the carbonyl group, CO, has the property of conferring acidity on neighbouring atoms of hydrogen, the basic qualities of only one of the two amido-groups, $-NH_2$, can display itself; hence the formula of the hydrochloride is $CO(NH_2)_2.HCl$, and not $CO(NH_2)_2.2HCl$, as might be expected. It is therefore a mono-acid base.

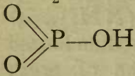
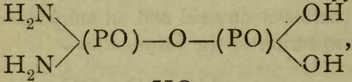
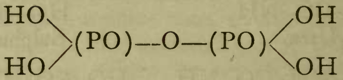
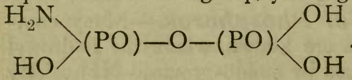
Urea can also be produced from inorganic sources, and it was the discovery of its synthesis from potassium cyanide by **Wöhler** in 1827 which caused the abandonment of the old view that compounds containing carbon, with the exception of its oxides, belonged to a special class, and could be produced only by the intervention of "life-power." Its production is as follows: Potassium cyanide is heated to redness with lead oxide; $KCN + PbO = KCNO + Pb$. The cyanate, KCNO, is next dissolved and mixed with a solution of ammonium sulphate, and the mixture is evaporated to dryness. It may be supposed that potassium sulphate and ammonium cyanate are first formed: $2KCNO + (NH_4)_2SO_4 = K_2SO_4 + (NH_4)CNO$. But the latter compound is unstable, and undergoes change into its isomeride, urea: $(NH_4)CNO = O=C(NH_2)_2$. On treatment with alcohol, insoluble potassium sulphate remains undissolved, while the soluble urea crystallises from the alcohol on evaporation. Urea is also produced when carbonyl chloride or when ethyl carbonate is treated with aqueous ammonia : $O{=}CCl_2 + 2NH_3 = O{=}C(NH_2)_2.HCl + HCl$; $O{=}C(OC_2H_5)_2 + 2NH_3 = O{=}C(NH_2)_2. + 2C_2H_5OH$. Lastly, carbamate of ammonium, when heated in a sealed tube, loses water with formation of urea : $H_2N{-}CO{-}ONH_4 = O{=}C(NH_2)_2 + H_2O$.

Biuret.—When urea is heated, a body named **biuret** is formed, with loss of one molecule of ammonia. We are here reminded of the relation between an acid and an anhydro-acid ; this is evident on inspection of the formulæ :—

$H_2N{-}CO{-}NH_2$ Urea.	$HO{-}SO_2{-}OH$ Sulphuric acid.
$H_2N{-}CO{-}NH{-}CO{-}NH_2$ Biuret.	$HO{-}SO_2{-}O{-}SO_2{-}OH$ Anhydrosulphuric acid.

Amides of Acids of Phosphorus.—Many compounds analogous to urea are known, where the hydroxyl groups of acids are replaced by amido-groups, $-NH_2$. By the action of ammonia gas on phosphorus oxychloride **ortho-phosphamide** is formed : $O{=}PCl_3 + 3HNH_2 = O{=}P(NH_2)_3 + 3HCl$. The ammonium chloride formed by the combination of the hydrochloric acid with excess of ammonia is removed by washing, and an insoluble white powder remains. When phosphamide is heated, ammonia is lost, and **phosphoryl-amide-imide** (the group $=NH$ is termed the "imido-group"), $HN{=}PO(NH_2)$, and at a higher temperature, $N{\equiv}P{=}O$ or **phosphoryl nitride** are left. They are also white insoluble powders. By analogy with carbamic acid and urea, there should exist compounds in which both hydroxyl and the amido-group are present. Some such compounds are known. **Thiophosphamic acid,** $S{=}P(NH_2)(OH)_2$, is the product of the action of ammonia on thiophosphoryl chloride ; and phosphoric anhydride, when dry ammonia gas is passed over it, yields **phosphimic acid,** thus : $P_2O_5 + 2NH_3 =$ 

$$\begin{matrix} O \\ NH \end{matrix} \!\!\gg\! P{-}OH$$

$+H_2O$. It is analogous to metaphosphoric acid,  $\left.\begin{array}{l}O\\O\end{array}\right\rangle P-OH$, and forms crystalline salts. **Pyrophosphamic** acids are also known. The addition of phosphoryl chloride to a cold saturated solution of ammonia results in the formation of pyrophospho-diamic acid  $\left.\begin{array}{l}H_2N\\H_2N\end{array}\right\rangle(PO)-O-(PO)\left\langle\begin{array}{l}OH\\OH\end{array}\right.$, analogous to pyrophosphoric acid,  $\left.\begin{array}{l}HO\\HO\end{array}\right\rangle(PO)-O-(PO)\left\langle\begin{array}{l}OH\\OH\end{array}\right.$; and on heating the solution of this body, one hydroxyl group replaces one amido-group, yielding **pyrophosphamic acid**,  $\left.\begin{array}{l}H_2N\\HO\end{array}\right\rangle(PO)-O-(PO)\left\langle\begin{array}{l}OH\\OH\end{array}\right.$. Lastly, the action of ammonia on phosphoric chloride gives a compound named phospham, $HN{=}P{\equiv}N$, a species of anhydride, but produced by loss of ammonia, not of water, from the unknown compound $P(NH_2)_5$.

Analogues of phosphorous acid are less well known; if ammonia be passed over phosphorous chloride, a white mass is formed, which has not been separated from ammonium chloride, but which is supposed to possess the formula $P(NH_2)_3$; it may be named **phosphorosamide**.

Amides of Sulphur Acids. — Similarly, amido-derivatives can be obtained from sulphur trioxide. The action of ammonia on that compound yields ammonium **sulphamate**, $H_4N{-}O{-}(SO_2){-}NH_2$, or, if less ammonia be used, **sulphamic acid**, $HO{-}(SO_2){-}NH_2$; they are both crystalline, soluble compounds.

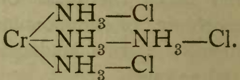
The action of sulphur dioxide on ammonia is accompanied by the production of the analogous compounds, **ammonium sulphurosamate** and **sulphurosamic acid**, the latter of which has the formula $HO{-}(SO){-}NH_2$.

These compounds may be taken as instances of bodies analogous to acids, in which the hydroxyl is replaced by the amido-group. They are, as a rule, stable in presence of water, and they do not generally unite with acids, the acid nature of the oxygen which they contain counteracting the basic nature of the amido-group. Many compounds are however known, in which the amido-group replaces hydroxyl, and which, having no acidic oxygen present, are known only as salts in combination with acids. Some of these will now be described.

Salts of Complex Amines. — Calcium chloride, exposed to a stream of ammonia gas, rapidly absorbs it, and forms the compound $CaCl_2.8NH_3$. It would appear that this compound is one of **calcamine**, $Ca(NH_2)_2$, with $2HCl$, with which six molecules of ammonia are associated in some manner resembling that in which water of crystallisation is associated in salts containing it. Thus we have $CaCl_2.6H_2O$; and $Ca(NH_3)_2Cl_2.6NH_3$ has an analogous formula. **Zinc** and **cadmium** form similar compounds, and other salts may be obtained from the appropriate salts of the metals; thus, by saturating zinc sulphate with ammonia, the compound $Zn(NH_3)_2SO_4.H_2O$ separates in crystals. Again, with aluminium, $Al(NH_3)_3Cl_3$ has been prepared; and dyad **iron, manganese,** and **nickel** yield somewhat similar compounds. Such bodies must be regarded as salts of ammonium, in which a metal has taken the place of one atom of hydrogen in each molecule of ammonium; a dyad metal replacing two metals in two molecules of ammonium, a triad three, and so on.

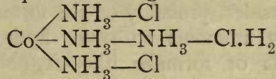
The **state of such compounds in solution** is probably that of "double salts," alluded to on pp. 10 and 161. While some of them are decomposed by water into ammonia and the salt of the metal, others resist that decomposition, and are ionised into complex groups, analogous to the platinichloride or the silicifluoride group. Thus, while it is probable that the compound of ammonia with calcium chloride in solution contains as ions $\overset{+}{Ca}$, $\overset{-}{Cl}$, $\overset{+}{NH_4}$, and $\overset{-}{OH}$, together with non-ionised NH_4OH and molecular NH_3, the fact that zinc hydroxide, precipitated by addition of ammonium hydroxide to a solution of the chloride, is re-dissolved by further addition of ammonia, is doubtless to be explained by the formation of the complex ion $Zn(NH_3)_2$, which is soluble in water. But this does not exclude the presence of the usual ions, $\overset{+}{Zn}$, $\overset{-}{Cl}$, $\overset{+}{NH_4}$, and $\overset{-}{OH}$, which doubtless co-exist with those already mentioned. In some cases, the stability of the complex ions is much greater than in that mentioned, and of this some instances will be given.

Chromamines.—**Chromium** hydroxide, when digested with excess of ammonia and ammonium chloride, forms a deep red solution; and on exposing it to air, a violet powder separates, of the formula $CrCl_3.4NH_3.H_2O$. This powder, heated to 100°, loses its water of crystallisation, and the residue has the formula $CrCl_3.4NH_3$. The ammonia is not expelled until the temperature 200° is reached. It would appear, therefore, that this compound is not $Cr(NH_3)_3.Cl_3.NH_3$, the fourth molecule of ammonia being regarded as of the same nature as water of crystallisation; it must rather be supposed that a complex ammonium group, $-NH_3-NH_3$, is capable of existence; whence the compound would have the formula



$$Cr\begin{cases}NH_3-Cl\\NH_3-NH_3-Cl.\\NH_3-Cl\end{cases}$$

Salts containing chromium have been prepared, in which 3, 4, 5, 6, and 7 molecules of ammonia are associated with the original chromium salt. They find their explanation by a hypothesis like the one given.

Cobaltamines.—Similar compounds are known with triad **cobalt**. On adding a solution of ammonia to cobalt sulphate, the precipitate at first formed (a basic sulphate) dissolves; exposure to air causes the oxidation of the cobalt from dyad to triad, and a black powder is deposited. On careful addition of hydrochloric acid, keeping the mixture cold, the colour of the powder changes to red; the compound has the formula  $Co\begin{array}{l} / NH_3—Cl \\ — NH_3—NH_3—Cl.H_2O \\ \backslash NH_3—Cl \end{array}$, and is analogous to the chromium compound mentioned above. Other salts of this base have been made; they are termed **roseo-cobaltamines.** If temperature be allowed to rise, during the addition of hydrochloric acid to the oxidised solution of cobalt sulphate in ammonia, an isomeric substance is produced, containing no water of crystallisation, and having a purple colour. Other salts are known; they are termed salts of **purpureo-cobaltamine.** It is possible to represent the formulæ of such compounds as follows:—

Diamines: $Cl\text{–}Co(NH_3)_2Cl_2$.
Triamines: $Co(NH_3)_3Cl_3$.
Tetramines: $Cl\text{–}Co(NH_3\text{–}NH_3)_2Cl_2$.
Pentamines: $NH_2\text{–}Co(NH\text{–}_3NH_3)_2Cl_3$.
Hexamines: $Co(NH_3\text{–}NH_3)_3Cl_3$.

Other Amines.—Many compounds of **copper, mercury, silver, gold,** and the metals of the **platinum** group are known, which admit of representation in a similar manner. They differ, however, inasmuch as the metal must be considered to have replaced more than one atom of hydrogen in one molecule of ammonium. Thus we have:

$Cu'_2{=}NH_2Cl$, **di-cuprosammonium chloride,** a black powder produced by the action of ammonia gas on warmed cuprous chloride:

$Cu'\text{–}NH_3Cl$, **cuprosammonium chloride,** formed by dissolving cuprous chloride in ammonia; it is a well-known absorbent for carbon monoxide and for acetylene.

$Cu''{=}(NH_3)_2Cl_2$, **cuprammonium chloride,** and **cupri-diammonium sulphate,** $Cu''{=}(NH_3\text{–}NH_3)_2SO_4$, the former a green substance, the latter a deep blue compound;

both produced by the action of ammonia on the respective cupric salt. The formation of the latter is a well-known test for copper.

With **silver** there are: **Argentamine**, a black explosive powder, probably of the formula $AgNH_2$, produced by adding ammonia to silver hydroxide; and numerous compounds of formulæ like $Ag(NH_3)Cl$, produced by dissolving the respective silver salts in ammonia. With **gold**: Auric chloride, digested with ammonia, yields "fulminating gold," an explosive black substance, which is a mixture of $HN{=}AuCl$ and $HN{=}Au{-}NH_2$.

A familiar test for mercurous mercury is to add ammonia, when the compound turns black. This is due to the formation of **di-mercurosammonium chloride**, or some similar compound, of the formula $Hg'_2{=}NH_2Cl$, where two atoms of hydrogen in ammonium chloride are replaced by two atoms of monad mercury. It has long been known, too, that mercuric salts produce a white precipitate on treatment with ammonia. This is chiefly due to the formation of **chloro-mercuramine**, $Cl{-}Hg''{-}NH_2$; here, the presence of electro-negative chlorine deprives the amido-group of basic properties. On boiling this compound with ammonium chloride, **mercurammonium chloride** is produced: $Cl{-}Hg{-}NH_2 + NH_4Cl = Hg(NH_3)_2Cl_2$.

With platinum, and the other members of that group, similar compounds are produced; but their constitution can be inferred sufficiently from what has preceded.

These compounds are derivatives of ammonia; there are few similar compounds of phosphine; one, however, is produced when phosphoretted hydrogen is passed over aluminium chloride; its formula is $PH_3.3AlCl_3$. And arsine, passed through a solution of mercuric chloride, yields $Hg_2AsCl.HgCl_2$; it is somewhat analogous to the black precipitate, $Hg_2NH.HCl$.

Phosphides, Arsenides, and Antimonides.—A few compounds of phosphorus, arsenic, and antimony with metals have been made. They are generally obtained by direct union between the heated metal and the element. Thus, if **sodium** and phosphorus be heated together under xylene, a hydrocarbon boiling about 130°, a black compound is formed, Na_3P, from which excess of phosphorus can be dissolved out by treatment with carbon disulphide. **Arsenide** and **antimonide** of **sodium** are also obtained by heating the elements together. The formulæ of these compounds are of the type $AsNa_3$; and with dilute acid, the corresponding hydride of phosphorus, arsenic or antimony is evolved: $AsNa_3 + 3HCl.Aq = AsH_3 + 3NaCl.Aq$. A mixture of **calcium phosphide,** Ca_3P_2, with calcium pyrophosphate is produced on throwing phosphorus into a crucible containing red-hot lime; on treatment with water, spontaneously inflammable phosphine is evolved. The spontaneous ignition is due to its containing P_2H_4, a liquid, very unstable compound.

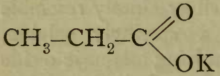
The **phosphides, arsenides,** and **antimonides** of the **other metals** are usually dark-coloured substances, with more or less metallic lustre, and therefore conductors of electricity. Some of them occur native; for example, **smaltine,** $CoAs_2$, a common ore of cobalt, forming silver-white crystals; **copper-nickel,** NiAs, red lustrous crystals, and one of the chief nickel ores; **speiss,** a deposit formed in the pots in which smaltine and copper-nickel are fused with potassium carbonate and silica, in the preparation of smalt, a blue glass containing cobalt; its formula appears to be Ni_3As_2. **Mispickel,** or **arsenical pyrites,** is a white lustrous substance, of the formula FeSAs.

Cyanides.—The elements carbon and nitrogen form a very stable group, of which the compounds have been well investigated, termed **cyanogen.** Carbon and nitrogen do not unite directly; but if a mixture of finely divided carbon with carbonate of potassium or sodium, or, better, of barium, be heated to about 1200° in a current of nitrogen, combination ensues, and a cyanide is formed, KCN, NaCN, or $Ba(CN)_2$; $BaCO_3 + 4C + N_2 = Ba(CN)_2 + 3CO$. **Potassium cyanide** is also produced when a mixture of animal refuse (horns, hides, hair, dried entrails, &c., of animals) with potassium carbonate and iron filings is heated. The nitrogen of the animal matter and the carbon unite with the potassium of the carbonate, forming cyanide. On addition of water, this cyanide reacts with salts of iron, forming a double cyanide of iron and potassium, termed "yellow prussiate of potash," or ferrocyanide of potassium, of the formula $K_4Fe(CN)_6$. When this compound is heated to dull redness, it fuses; a black mixture or compound of iron and carbon remains, and melted potassium cyanide can be poured out of the crucible. Potassium cyanide, KCN, is a very soluble salt; it crystallises well from alcohol. Its solution smells of hydrocyanic acid; this is because it is hydrolysed by water. The acid, HCN, is so very weak that the number of hydrogen ions present in its solution are comparable in number with those of ionised water; hence the change: $\overset{+}{H}-\overset{-}{O}H + \overset{+}{K}-C\overset{-}{N}.Aq = HCN + \overset{+}{K}\overset{-}{O}H.Aq.$ The ionised portion of the hydrocyanic acid is as usual non-volatile; but the non-ionised portion has a vapour-pressure, and can be detected by its smell (cf. p. 141).

Hydrocyanic Acid.—Inasmuch as **hydrocyanic** or "prussic" **acid** is so very weak, it is displaced from its salts by the action of all other acids; even carbonic acid can expel it. It may therefore be prepared by distilling a cyanide (potassium cyanide or ferro-cyanide is generally used) with dilute sulphuric acid. The vapour comes off along with water; to remove the water, if the anhydrous acid is required, the mixture of vapours may be passed through a tube charged with dry calcium chloride, which retains the water; or by another method, mercuric cyanide may be decomposed by passing over it a current of dry sulphuretted hydrogen, the excess of which is removed by causing the gases to traverse a tube filled with lead carbonate; the hydrocyanic acid must be condensed in a freezing-mixture, for it boils at 27°. The solid compound melts at −15°. All experiments with anhydrous or with concentrated hydrocyanic acid must be carried out in a good draught-chamber, for it is the most poisonous substance known, and a breath of its vapour has been attended by fatal effects.

The **cyanides** are produced by addition of the oxides or hydroxides to hydrocyanic acid. Those of the **alkalies** and **alkaline earths** are white, soluble crystalline compounds; those of lead, mercury, and silver closely resemble the chlorides. Mercuric cyanide, a sparingly soluble, white crystalline salt, is formed by dissolving mercuric oxide in hydrocyanic acid; lead cyanide is also sparingly soluble, and silver cyanide, produced by addition of potassium cyanide to a soluble silver salt, is an insoluble white precipitate, undistinguishable from silver chloride in appearance. The cyanide of silver or of mercury, when heated, yields **cyanogen**, $(CN)_2$, a colourless gas, possessing the characteristic cyanide smell, somewhat resembling that of bitter almonds. Like hydrocyanic acid, it is very poisonous. It burns with a blue-purple flame; it is fairly soluble in water and in alcohol. It condenses to a liquid which boils at $-20°$, and freezes at $-34.4°$. It is an endothermic substance, being formed from its elements with an absorption of heat of $-65,700$ calories.

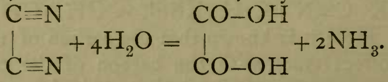
Isomeric Cyanides.—The **formula** of **hydrocyanic acid** can be represented in two ways. It is possible to conceive either the carbon or the nitrogen to be united with the atom of hydrogen. In the former case, the structural formula is $H{-}C{\equiv}N$; in the latter, $H{-}N{\equiv}C$. There is no method of determining which of the two formulæ is to be ascribed to the acid or to its simple salts; but salts with alcohol radicals are known to which one or other formula can be ascribed. On distilling potassium cyanide with potassium ethyl-sulphate, the following change takes place: $K{-}C{\equiv}N + C_2H_5.KSO_4 = CH_3{-}CH_2{-}C{\equiv}N + K_2SO_4$. Here it is known that the carbon of the ethyl group is in direct union with the carbon of the cyanogen for two reasons: first, when ethyl cyanide is exposed to the action of nascent hydrogen (*e.g.* treated with tin and hydrochloric acid) hydrogen adds itself both to the carbon and to the nitrogen of the cyanide group, and propylamine, $CH_3{-}CH_2{-}CH_2{-}NH_2$, is formed ; and second, on boiling ethyl cyanide with a solution of caustic potash in alcohol, an acid with three carbon atoms, propionic acid, is formed : $CH_3{-}CH_2{-}C{\equiv}N + KOH + H_2O =$



$$CH_3{-}CH_2{-}C\begin{cases} {=}O \\ {-}OK \end{cases} + NH_3$$

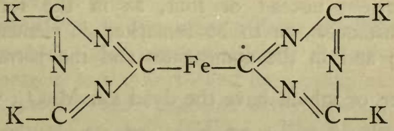
; dyad oxygen and monad potassoxyl replace triad nitrogen. On the other hand, if ethyl iodide, $CH_3{-}CH_2{-}I$, be boiled in alcoholic solution with silver cyanide, the change is : $CH_3{-}CH_2{-}I + Ag{-}N{\equiv}C = CH_3{-}CH_2{-}N{\equiv}C + AgI$. Here the nitrogen is in direct union with the carbon atom of the ethyl group ; this is known because on boiling the compound with dilute acid, hydrolysis takes place, thus : $CH_3{-}CH_2{-}N{\equiv}C + 2H_2O = CH_3{-}CH_2{-}NH_2 + H{-}CO{-}OH$; the nitrogen remains in union with the carbon. Hence it is concluded that while potassium cyanide must contain $K{-}C{\equiv}N$, along with $K{-}N{\equiv}C$ (for both compounds are formed by the first action), silver cyanide consists almost exclusively of $Ag{-}N{\equiv}C$. The name applied to the first compound, CH_3CH_2CN, is ethyl cyanide, or, preferably, propionitrile, seeing that it differs from propionic acid only in having nitrogen in place of oxygen and hydroxyl ; while the latter is turned ethyl isocyanide or ethyl carbamine, for it contains carbon replacing hydrogen in ethylamine, $CH_3CH_2{-}NH_2$.

Hydrocyanic acid may on the same grounds be termed "formonitrile," for, on standing with dilute acid, it is converted into formic acid by assumption of the elements of water : $H{-}C{\equiv}N + 2H_2O = H{-}CO{-}OH + NH_3$; and cyanogen, for the same reasons, may be named "oxalonitrile" :



$$\begin{matrix} C{\equiv}N \\ | \\ C{\equiv}N \end{matrix} + 4H_2O = \begin{matrix} CO{-}OH \\ | \\ CO{-}OH \end{matrix} + 2NH_3.$$

Ferro- and Ferricyanides.—Some of the double cyanides are of importance, both commercially and from a chemical standpoint. Among them is a substance which has already been mentioned, **potassium ferrocyanide,** $K_4Fe(CN)_6$. This compound forms large yellow tabular crystals; it contains ferrous iron, hence the name ferro(us)cyanide. It is supposed to be derived from a tricyanogen group, and to have the formula



The ions of this salt are five, viz., $4\overset{+}{K}$, and the complex group $\overset{----}{Fe(CN)_6}$; the fall in freezing-point of an aqueous solution caused by the presence of a gram-molecule in 100,000 parts of water, and the conductivity of a similarly dilute aqueous solution indubitably indicate the presence of five ions. Moreover, the salt shows none of the reactions characteristic of ions of dyad iron, such as precipitation as sulphide on addition of ammonium sulphide, precipitation as hydroxide on addition of alkalies, &c. The acid corresponding to this salt, **hydroferrocyanic acid,** $H_4Fe(CN)_6$, can be prepared by adding to a boiled solution of potassium ferrocyanide concentrated hydrochloric acid and a little ether; it precipitates in white crystals. The **zinc** salt and the **copper-potassium** salt, $K_2CuFe(CN)_6$, are insoluble; the former is white, and the latter a slimy brown-red precipitate.

On passing a current of chlorine through a solution of potassium ferrocyanide, or on submitting it to the action of any oxidising agent, **potassium ferri(c) cyanide** is formed: $2K_4Fe(CN)_6 . Aq + Cl_2 = KCl . Aq + 2K_3Fe(CN)_6 . Aq$. The new compound contains ferric iron, hence its name; the "c" is omitted for the sake of euphony. This salt crystallises in dark red prisms, and dissolves in water with an orange colour. The acid, prepared from the lead salt, which is sparingly soluble, by the action of dilute sulphuric acid, and evaporation to crystallising point, forms brownish needles. Here again the complex group $-\overset{---}{\mathrm{Fe}(\mathrm{CN})_6}$ is one of the complex ions in solution along with $3\overset{+}{\mathrm{K}}$; and it is to be noticed that it now carries only three electrons instead of four, as in the ferrocyanide. Similar instances are to be remarked in elements of two valencies; and in the manganates and the permanganates, the former of which have the dyad ion $\overset{--}{\mathrm{MnO}_4}$, while with the latter it is monad, $\overset{-}{\mathrm{MnO}_4}$. The iron salts of ferro- and ferricyanic acids are especially interesting, and some of them are of commercial importance. On adding a solution of ferrocyanide of potassium, boiled so as to expel dissolved oxygen, to a solution of iron wire in sulphurous acid, which is also free from dissolved oxygen, a white precipitate of **potassium ferrous ferrocyanide** results: $\mathrm{FeSO_3.Aq} + \mathrm{K_4Fe''(CN)_6.Aq} = \mathrm{K_2Fe''Fe''(CN)_6} + \mathrm{K_2SO_3.Aq}$. If these precautions to exclude oxygen are not taken, the precipitate is light blue in colour, and is a common test for ferrous iron. This compound is also formed when ferrocyanide of potassium is distilled with dilute sulphuric acid, as in the preparation of prussic acid: $2\mathrm{K_4Fe''(CN)_6.Aq} + 3\mathrm{H_2SO_4.Aq} = \mathrm{K_2Fe''Fe''(CN)_6} + 3\mathrm{K_2SO_4.Aq}$. When boiled with dilute nitric acid, the white compound is converted into a blue soluble compound, which may be regarded either as **potassium ferrous ferricyanide** or **potassium ferric ferrocyanide**, $\mathrm{KFe''Fe'''(CN)_6}$, or $\mathrm{KFe'''Fe''(CN)_6}$. This same compound is produced also by the addition of a ferric salt to potassium ferrocyanide: $\mathrm{K_4Fe''(CN)_6.Aq} + \mathrm{Fe'''Cl_3.Aq} = \mathrm{KFe'''Fe''(CN)_6.Aq} + 3\mathrm{KCl.Aq}$; or by adding a ferrous salt to potassium ferricyanide: $\mathrm{K_3Fe'''(CN)_6.Aq} + \mathrm{Fe''Cl_2.Aq} = 2\mathrm{KCl.Aq} + \mathrm{KFe''Fe'''(CN)_6.Aq}$. When mixed with excess of a ferrous salt, it gives a blue precipitate named

"**Turnbull's blue**": $2KFe''Fe'''(CN)_6.Aq + Fe''SO_4.Aq = Fe''_3Fe'''_2(CN)_{12}$; and with excess of a ferric salt, "**Prussian blue**" is formed: $3KFe''Fe'''(CN)_6.Aq + Fe'''Cl_3.Aq = Fe''_3Fe'''_4(CN)_{18} + 3KCl.Aq$. Potassium ferricyanide, with ferric iron, gives a brown solution, which may contain ferric cyanide. These colours are used as tests for ferric or ferrous iron.

Chromicyanides, manganicyanides, cobalticyanides, ruthenocyanides, and **osmocyanides,** are also known, similar in formulæ to the ferro- and ferri-cyanides. On the other hand, nickel and platinum form double cyanides similar in formula to $K_2Pt(CN)_4$. The **platinum** salts are very beautiful, possessing the property of dichroism, *i.e.* of transmitting light different in colour from that which the crystals reflect; moreover, only some of the facets of the crystals have this property.

Silver cyanide is soluble in a solution of potassium cyanide, also forming a double salt, of the formula $KAg(CN)_2$. Here the ions are $\overset{+}{K}$ and $\overset{-}{Ag(CN)_2}$. This salt finds two uses. First, it is the compound from which silver is best deposited electrolytically in electroplating (see p. 10). **Potassium auricyanide,** $\overset{+}{K}\overset{-}{Au(CN)_4}.Aq$, produced by the addition of auric chloride, $AuCl_3$, to a solution of potassium cyanide, is employed in gold-plating. Second, the existence of the soluble ion, $Ag(CN)_2$, furnishes a means of estimating the amount of hydrocyanic acid in a dilute solution such as is used for medicinal purposes. A decinormal solution of silver nitrate, that is, one containing one-tenth of the molecular weight of the salt taken in grams, or 17 grams per litre, will react with 13.02 grams of potassium cyanide, or with 5.4 grams of hydrocyanic acid, forming the double salt, thus: $\underset{170}{AgNO_3.Aq} + \underset{130.2}{2KCN.Aq} = KNO_3.Aq + KAg(CN)_2.Aq$. The solution of silver nitrate is added from a measuring-tube or burette until a faint trace of turbidity begins to appear ; this signifies that the reaction given above has completed itself, and that the second reaction—$\text{KAg(CN)}_2\text{.Aq} + \text{AgNO}_3\text{.Aq} = \text{KNO}_3\text{.Aq} + 2\text{AgCN}$—has just begun. Every cubic centimeter, therefore, of silver nitrate added corresponds to the presence of 0.0054 grams of hydrocyanic acid in solution.

Metallic gold is soluble in a dilute solution of potassium or sodium cyanide, the complex group Au(CN)_3 being formed, thus :—

$$4\text{KCN.Aq} + \text{Au} = \text{KAu(CN)}_4\text{.Aq} + \text{K}.$$

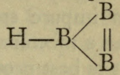
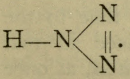
The action of the potassium on the water is to liberate hydrogen. But this hydrogen attacks the oxygen *dissolved* in the water, and is removed by water. The process is largely used in recovering gold from poor gold ores, or from the "slimes," or mud left after removing the bulk of the gold from the crushed ore, by amalgamating it with mercury.

The addition of a solution of potassium cyanide to a solution of a cupric salt in ammonia, which, it will be remembered, contains the blue ions of the cupramine, $\overset{+\ +}{\text{Cu}(\text{NH}_3)_2}$, decolorises the solution. This is due to the formation of the double salt, **potassium cupricyanide**, $\overset{+}{\text{K}}_2\overset{-\ -}{\text{Cu}(\text{CN})_4}\text{.Aq}$, the ions of which are colourless. The copper is not present in the form of cupric ions, $\overset{++}{\text{Cu}}$, hence it does not give the reactions characteristic of these ions. For example, it yields no precipitate with sulphuretted hydrogen ; and this affords a means of separating copper from cadmium, which is unaffected by addition of potassium cyanide.

CHAPTER X

Borides and Carbides—Alloys: their classification—The commoner Alloys.

Borides and Carbides.—These compounds have been incidentally mentioned on p. 30; they have been investigated almost exclusively by **Moissan** and his pupils.

Borides.—**Calcium**, **strontium**, and **barium borides** have been prepared by heating in an electric furnace a mixture of borate of the metal with aluminium filings and carbon. At the high temperature of the electric arc the carbon reduces the aluminium oxide and prevents its formation. These compounds form hard, transparent microscopic cubes, burning only when maintained at a red heat in oxygen, and attacked with difficulty by the halogens. Their formulæ are curious; they are analogous to the very unstable hydrazoates, $M'(N)_3$, being $Ca(B_3)_2$, $Sr(B_3)_2$, and $Ba(B_3)_2$; and their existence would point to a supposititious compound of the formula  like .

Ferric boride, produced by heating together boron and wrought-iron in an electric furnace, consists of brilliant yellowish-grey crystals, burning brilliantly when heated in oxygen, and attacked by nitric acid. The corresponding compounds of **nickel** and **cobalt**, prepared in the same manner, form brilliant prisms. The formulæ are FeB, NiB, and CoB.

Carbon boride, CB_6, forms lustrous black crystals, nearly as hard as diamond, on which facets can be cut by its use; it is produced by heating a mixture of amorphous boron and sugar-charcoal in the electric furnace.

Carbides.—**Lithium carbide,** Li_2C_2, is a white crystalline mass, produced by heating in the electric furnace a mixture of carbon with lithium carbonate; its formation is expressed by the equation: $Li_2CO_3 + 4C = Li_2C_2 + 3CO$. It is decomposed at a temperature not much higher than that at which it is formed; hence the exposure to the high temperature of the electric furnace should be only a short one. The analogous compounds of **sodium** and **potassium** do not resist such a high temperature; they must therefore be prepared by exposing the metal for several weeks to the action of acetylene under pressure. This process yields compounds of the formulæ $NaHC_2$ and KHC_2; when heated, they change, with evolution of acetylene, into the carbides Na_2C_2 and K_2C_2. Like lithium carbide, they are white crystalline substances, and with water acetylene is evolved: $Na_2C_2 + 2H_2O = 2NaOH + C_2H_2$.

Calcium carbide, CaC_2, has attained great industrial importance owing to its serving as the source of acetylene, now largely used for illuminating purposes. It was made in an impure state in 1892 by **Travers** by heating together a mixture of calcium chloride, carbon, and sodium; but it is best produced by **Moissan's** process in the electric furnace, by heating a mixture of carbon and lime to the very high temperature (about 3000°) obtained in that manner. It forms blackish-grey, lustrous crystals, at once attacked by water: $CaC_2 + 2HOH = C_2H_2 + Ca(OH)_2$. **Carbides of strontium** and **barium** are made in a similar manner, and have properties analogous to those of the calcium compound.

Other carbides prepared by Moissan in a crystalline state by means of the electric furnace are: CeC_2, LaC_2, YC_2, ThC_2, which yield with water a mixture of acetylene, ethylene, methane, and hydrogen; Al_4C_3, which is decomposed by water, yielding pure methane; Mn_3C, yielding methane and hydrogen; and U_2C_3, the products from which are ethylene, methane, and hydrogen. By heating the oxide of the respective metal with calcium carbide, the carbides Cr_3C_2, Mo_2C, W_2C, TiC, and SiC have also been prepared. The last of these has become known commercially under the name "**carborundum.**" It forms extremely hard, blackish-blue, hexagonal crystals; when pure it is colourless. It is prepared on a large scale by heating together in the electric furnace a mixture of carbon (coke) and white sand. It is used for grinding and polishing metals and glass.

Steel, as is well known, differs from iron by the presence of a certain amount of carbon, which induces the iron, when cold, to persist in its allotropic state. This appears to be due to a **carbide** of **iron** mixed with the excess of iron in the steel. The compound has been found as a meteoric mass; it has been named **cohenite**, and has the formula Fe_3C. On treating steel with dilute acetic acid, the same substance remains as a black powder. Its formula is similar to that of manganese carbide, Mn_3C.

Silicides.—Some silicides have also been prepared by aid of the electric furnace by heating elements with silicon. Among these are Fe_2Si, lustrous prisms; Cr_2Si, Ni_2Si, Co_2Si, Mn_2Si, Cu_2Si, and Pt_2Si, with similar properties. **Magnesium silicide**, Mg_2Si, prepared by heating a mixture of powdered silica and magnesium dust to redness, is attacked by dilute acid, evolving a mixture of hydrogen and hydrogen silicide (see p. 38).

Alloys.—The word "alloy" was originally applied to mixtures of gold and silver with other metals; it now signifies any mixture or compounds of metals with each other; alloys of mercury are, however, termed "amalgams." When two metals are melted together, they always mix, more or less. Some may be mixed in any desired proportion, such as lead and tin; others are partially soluble in each other; zinc, for example, dissolves 1.6 per cent. of lead, and lead 1.2 per cent. of zinc; but on stirring up the metals together, there is always a layer at the top of the lighter alloy of zinc with lead, and below it the heavier alloy, consisting chiefly of lead. By raising the temperature the mutual solubility of the metals increases, and at a sufficiently high temperature it is probable that they would mix completely.

Classification.—Alloys in general may be classified under two heads: (1) definite compounds, in which the elements are present in atomic proportions; and (2) mixtures in which combination has not taken place. To these classes may be added a third—mixtures of definite compounds with one or other of the components of the alloy. As such mixtures are usually homogeneous, it is often a matter of great difficulty to identify the definite compounds. In many cases, too, it would appear that one of the metals in the alloy is present in an allotropic form; for example, on treatment of one of the alloys of rhodium and zinc with dilute hydrochloric acid, after solution of the zinc, the rhodium is left in an allotropic form.

The **constitution of alloys** can be deciphered by several processes. One depends on measurement of the electromotive force of a battery consisting of the alloy and a plate of some resistant metal—for instance, platinum—compared with that of a similar cell made with one of the constituents of the alloy. To take a concrete example. Suppose a cell were constructed of a plate of copper and a plate of platinum dipping in some appropriate liquid, a certain electromotive force would result. Imagine a plate of tin riveted to the face of the copper plate, the electromotive force would now be that of the more electropositive metal, tin. If a plate of bronze be substituted, supposing it to contain free tin not in chemical combination with the copper, then the electromotive force will still be that of tin against platinum. A chemical compound of tin and copper, however, would have a less electromotive force than free tin; and as the tin in the alloy mentioned is dissolved away, the electromotive force will suddenly fall when the excess of tin has been dissolved, until it is equal to that of the chemical compound against platinum. An analysis of the alloy at this stage will reveal the composition of the compound. In this way the existence of a compound of the formula Cu_3Sn was detected.

The second method of determining whether an alloy contains a definite compound is to compare the freezing-points of various alloys of the metals. The presence of a small amount of one metal in another in general lowers the freezing-point; and the freezing-point is continuously lowered by successive additions, until the lowering reaches a maximum. The mixture which has the lowest possible melting-point is termed the "eutectic" alloy. The composition of this alloy does not necessarily coincide with that of a definite compound; indeed, metals which form no compound with each other exhibit this phenomenon. If a compound is formed, however, the melting-point rises to a maximum on continuous addition of the second metal, and that compound which has the highest melting-point corresponds with a definite formula. Further addition of the second metal causes a lowering of the freezing-point of the definite compound; and this lowering increases on addition of the second metal, until a second eutectic alloy is formed, one consisting of a mixture of the compound with excess of the second metal. Further addition of the second metal now causes the melting-point to rise, it may be to the melting-point of the second metal; in that case only one compound of the two metals is capable of existence. It may happen, however, that, after rising to a certain temperature, the temperature again falls on addition of more of the second metal; in that case, the highest temperature reached corresponds to the existence of a second compound; a similar change may even denote the existence of a third. By such means it is possible to detect the existence of definite compounds between any two metals. With ternary alloys, *i.e.* with alloys containing three metals, although the phenomenon is more complicated, this method has led to the discovery of several definite compounds.

While alloys have generally been prepared by melting the metals together, or by melting one of them and adding the other, some alloys have been produced by submitting mixtures of the metallic powders to enormous pressure.

"**Fusible Alloys.**"—Among the eutectic alloys, some are known as "fusible alloys." "Wood's alloy" consists of two parts of tin, two of lead, seven or eight of bismuth, and one or two of cadmium; it melts at 66°–71°; an alloy melting at 60° (Lipowitz's) consists of tin four parts, lead eight parts, bismuth fifteen parts, and cadmium three parts.

Among the few alloys of **definite composition** are: $ZnPt$, Zn_3Hg, Cd_2Tl, Al_3Mn, Sn_4Pt, Cu_3Sn, and $PtHg_2$. Attempts have been made to separate the constituents of alloys by passing a current of high potential through the melted alloy, with the expectation that electrolysis would take place; but no sign of such separation could be detected; the alloy conducts as a whole.

The following alloys, among others, find practical use:—

Sodium amalgam, made by adding small pieces of sodium to mercury, warmed under a layer of heavy paraffin oil; it is liquid when it contains under 1.5 per cent. of sodium, and solid if it contains more. It is used as a source of nascent hydrogen, for it is slowly attacked by water, and more rapidly by dilute acids. On adding this alloy to a concentrated solution of ammonium chloride, a very remarkable phenomenon takes place; the amalgam swells up enormously while retaining its metallic appearance; the product is soft and of buttery consistency; it may consist of **ammonium amalgam**, and may contain the complex group NH_4, or, more probably, $(NH_4)_2$. On standing, it rapidly decomposes into mercury, ammonia, and hydrogen.

The addition of a little **magnesium** to **nickel** lowers its melting-point considerably, and renders it ductile and malleable. A similar addition of a little **aluminium** to **iron** also improves the qualities of the iron. The product is called "Mitis steel."

"**Galvanised iron**" is produced by passing clean sheets of iron through molten zinc. Alloying takes place on the surface of the iron. Such plates, in a corrugated form, are largely used for roofing buildings. As zinc is a more electropositive metal than iron, the iron is thereby protected from rusting. Iron is similarly coated with **tin**; but in this case, the iron, if exposed, is prone to rust, for iron is more electropositive than tin, and is attacked by carbonic acid in water more readily than the tin. Indeed, rusting proceeds in an accelerated rate owing to the presence of the tin, for the two metals form a couple.

To deprive commercial **lead** of the **silver** which it almost always contains, zinc is stirred up with the molten metal; the zinc dissolves the silver and floats to the surface of the lead; it is allowed to harden, and the cake is then removed. The silver and zinc are separated by distillation of the more volatile zinc; the lead is freed from zinc by melting it in an oxidising atmosphere, when the more easily oxidisable zinc is first oxidised, and can be removed as dross. This is Parke's process for desilverising lead.

The alloy of **zinc** with **copper** is termed **brass**, **pinchbeck**, **Muntz metal**, and **tombac**. English brass usually contains 70 per cent. of copper and 30 of zinc. It is made by melting the copper and adding the molten zinc. The addition of **nickel** (Cu 52 per cent., Zn 23 per cent., Ni 15 per cent.) yields "**German silver**," of which spoons, forks, and coins are made. Electroplate has usually a basis of this alloy, and is covered with silver by depositing it from its double cyanide with potassium. Zinc coated over with a superficial layer of **zinc amalgam** is not attacked by dilute sulphuric acid, and is therefore used as the negative pole of most batteries; it is only on connecting with some less electropositive metal that hydrogen is evolved from the latter, while the zinc dissolves.

"**Aluminium bronze**" is an alloy of **aluminium** with **copper**, containing from 2 to 11 per cent. of the former metal. It resembles gold in colour, and is employed in the manufacture of imitation jewellery.

"**Ferrochrome**" and "**ferromanganese**" are produced by simultaneous reduction of ores of iron and chromium, or of iron and manganese. Their addition in small quantity to iron improves its quality. Iron containing about 10 per cent. of manganese is known as "**spiegel iron**," for it crystallises in large brilliant plates. Tungsten, too, is sometimes added to iron to increase its hardness.

"**Pewter**" is an alloy of 80 per cent. of **lead** with 20 per cent. of **tin**; **plumbers' solder** consists of two parts of lead to one of tin; "**Britannia metal**" is made of equal parts of brass, tin, antimony, and bismuth.

"**Bronze**" is one of the most ancient alloys, and used to be made by reducing together copper ores and tin ores. It often contains twenty-two parts of **tin** and seventy-eight parts of **copper**. Its hardness is greatly increased by the presence of a trace of phosphorus. "Speculum metal," for astronomical mirrors, is made by alloying thirty-two parts of tin with sixty-seven of copper and one of arsenic. It takes a very high polish. Copper is easily tinned by melting the tin in the vessel, and pouring out the excess; this is frequently done to vessels required for cooking.

"**Type-metal**" is an alloy of **lead** and **antimony**, containing 18 per cent of the latter. It expands slightly on solidifying, and consequently when cast in the mould it takes an accurate impression and forms a clean-cut type.

The "**Pattinson's process**" is a rival of the Parke's process in desilverising crude lead. The lead is melted and allowed to solidify partially; the solid portion consists of nearly pure lead. The liquid portion contains the silver. By repetition of the process, the lead may be nearly completely deprived of silver; and an alloy rich in silver may be obtained, from which the lead may be removed by cupellation.

Osmiridium is a native alloy of osmium and iridium; it is extremely hard, and it is used for pointing gold pens and for the bearings of small wheels. An alloy of platinum with 10 per cent. of iridium is the metal employed for crucibles.

An alloy of **copper** and **silver** is used for coinage; English coins contain 7.5 per cent. of copper. The alloy must be rapidly cooled, else it ceases to be homogeneous. **Gold** is also alloyed with **copper** for coinage; pure gold is a soft metal. The English standard is eleven parts of gold to one of copper; in France and the United States, nine of gold to one of copper. The richness of such an alloy is measured in "carats." Pure gold is "24-carat gold;" "18-carat gold" contains eighteen parts of gold and six of copper.

The study of the chemistry of metallic alloys was for long neglected, but of recent years much has been done. It is curious to think that the successful solution of many chemical problems is to be expected from careful examination of this class of substances, which was the first to engage the attention of the chemists of the remote past.

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THE END

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